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BD/DE/SAC/21-27

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3. Full name, address and postcode of the or of each applicant (underline all surnames)

UNIVERSITY OF WARWICK

Gibbet Hill Road
Coventry
CV4 7AL

Patents ADP number (if you know it)

4019162001

If the applicant is a corporate body, give the country/state of its incorporation

UK

4. Title of the invention

POLYMERISATION CATALYST AND PROCESS

5. Name of your agent (if you have one)

WITHERS & ROGERS

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04/04/97

B. J. N. Dempster

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POLYMERISATION CATALYST AND PROCESS

The present invention relates to a process for the free radical initiated polymerisation of olefinically unsaturated monomers in which molecular weight control is achieved by the presence of certain transition metal, especially copper, diimine complexes. These copper complexes can be formed with either by reaction of copper(I) salts with appropriate diimines in situ or the isolated copper-diimine complex may be used. Copper(I) diimine complexes are used in conjunction with an appropriate alkyl halide.

It is desirable to be able to produce high molecular weight polymers with a low molecular weight distribution by catalysed addition polymerisation by a free radical process, in particular of vinylic monomers. Hitherto this has been achieved by polymerising via ionic processes typically in the presence of organometallics such as alkyl lithium's which are sensitive as regards reaction with water and other protic species. As such monomers containing functional groups are not readily polymerised. The use of ionic systems also precludes the use of solvents which contain protic groups and/or impurities resulting in very stringent reaction conditions and reagent purity being employed.

More recently systems based on the combination of a transition metal halide and alkyl halide have been utilised. For example Matyjasewski (Macromolecules (1995), vol 28, pages 7901-7910) has described the use of CuX (where X=Cl, Br) in conjunction with bipyridine and an alkyl halide to give polymers of narrow molecular weight distribution and controlled molecular weight. This system suffers from the disadvantage that the copper catalyst is only partially soluble in the system and thus a heterogeneous polymerisation ensues. The level of catalyst which is active in solution is thus difficult to determine. Precec Macromolecules, (1995), vol. 28, page 1995) has extended Matyjasewski's work by utilising arenesulphonyl chlorides to replace alkyl chlorides, again this results in heterogeneous polymerisation. Sawamoto (Macromolecules, (1995), vol. 28, page 1721) has also utilised a ruthenium based system for similar polymerisation of methacrylates. This system requires activation of monomer by aluminium alkyl, itself sensitive to reaction with protic species which is an inherent disadvantage.

Surprisingly the inventors have found that the use of diimines such as 1,4-diaza-1,3-butadienes and 2-pyridinecarbaldehyde imines may be used in place of bipyridines. These ligands offer the advantage of homogeneous polymerisation and thus the level of active catalyst can be accurately

controlled. This class of ligand also enables the control of the relative stability of the transition method valencies, for example, Cu(I) and Cu(II), by altering ancillary substituents and thus gives control over the nature of the products through control over the appropriate chemical equilibrium.

5 Such a system is tolerant to trace impurities, trace levels of O_2 and monofunctional monomers, and may be conducted in aqueous media.

Accordingly a first aspect of the invention provides a catalyst for addition polymerisation of olefinically unsaturated monomers, especially vinylic monomers, comprising:

10 a) a first compound of formula I



where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and X is a monovalent anion:

15 b) a second compound of general formula II



where R = straight or branched alkyl C_nH_{2n+1} , where n is a whole number, benzyl $PhCH_2$, substituted alkyl, or substituted benzyl and x = Cl, Br, I; and

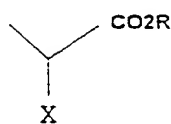
20 c) an organodiimine.

Transitional metals may have different valencies, for example Fe(II) and Fe(III), Cu(I) and Cu(II), a low valency state is the lower of the commonly occurring valencies, i.e. Fe(II) or Cu(I). Hence M in Formula I is preferably Cu(I), Fe(II), Co(II), Ru(II) or Ni(II), most preferably Cu(I).

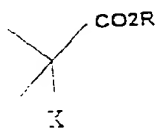
5 Preferably the co-ordinating ligand is $\text{Cu}(\text{CH}_3\text{CN})_4$. X may be chosen from Cl, Br, I, NO_3 , PF_6 or BF_4 .

Preferably the second component (b) is selected from

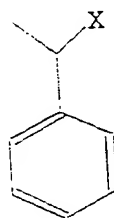
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Formula III



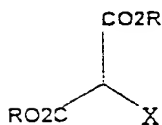
Formula IV



Formula V

or

15



Formula VI

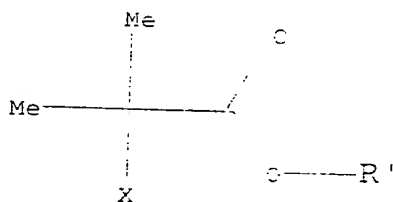
20

where R is independently selectable and is as defined previously.

Preferably $n = 1$ to 20, more preferably 1 to 10, especially 1 to 5.

Preferably the substituted alkyl group contains 1 to 20, preferably 1 to 10, especially 1 to 5 carbon atoms.

5 The second component (b) may also have Formula XIII



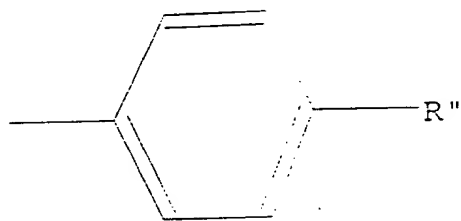
10 where:

$X = \text{Br, I or Cl, preferably Br}$

$R' = -\text{H,}$

$-(\text{CH}_2)_m R''$ (where m is a whole number, preferably $m = 1$ to 20, more preferably 1 to 10, most preferably 1 to 5)

15 or

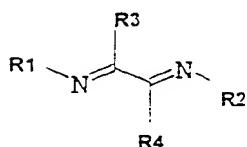


20 $R'' = -\text{COOH, -COX (where X is Br, I or Cl), -OH, -NH}_2 \text{ or -SO}_3\text{H.}$

Most preferably b is 2-hydroxyethyl-2'-methyl-2' bromopropionate.

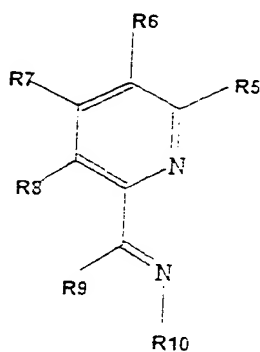
The careful selection of functional alkyl halides allows the production of terminally functionalised polymers. For example, the selection of a hydroxy containing alkyl bromide allows the production of x-hydroxy terminal polymers. This can be achieved without the need of protecting group chemistry.

Component (c) may be selected from 1,4-diaza-1,3-butadiene



Formula VII

or a 2-pyridinecarbaldehyde imine



Formula VIII

where R_1 , R_2 and R_{10} may be varied independently and R_1 , R_2 and R_{10} may be H, straight chain or branched chain saturated alkyl, aryl (such as phenyl or phenyl substituted where substitution is as described for R_4 to R_9), CH_2Ar (where $\text{Ar} = \text{aryl}$) or a halogen. Preferably R_1 , R_2 and R_{10} may be a C_1 to C_{20} alkyl, in particular C_1 to C_4 alkyl, methylmethacrylate, ethylmethacrylate, n-propylisopropyl, n-butyl, sec-butyl, tert butyl, cyclohexyl, 2-ethylhexyl, octyl decyl or lauryl. R_1 , R_2 and R_{10} may especially be methyl.

10

R_3 to R_9 may independently be selected from the group described for R_1 , R_2 and R_{10} or additionally OCH_{2n-1} (where n is an integer from 1 to 20), NO_2 , CN or $\text{O}=\text{CR}$ (where $\text{R} = \text{alkyl}$, benzyl PhCH_2 or a substituted benzyl).

15

Compounds of general Formula VIII may comprise one or more fused rings on the pyridine group.

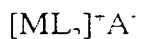
20

Adjacent R_1 and R_3 , R_3 and R_4 , R_4 and R_2 , R_{10} and R_9 , R_8 and R_9 , R_8 and R_7 , R_7 and R_6 , R_5 and R_5 groups may be C_5 to C_8 cycloalkyl, C_5 to C_8 cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, such as

cyclohexyl, cyclohexenyl or norborneyl.

A second aspect of the invention provides a catalyst for addition
polymerisation of olefinically unsaturated monomers, especially vinylic
monomers, comprising:

a first component of Formula XI



wherein M = a transitional metal in a low valency state;

L = an organodiimine

A = a monovalent anion.

(e) A second component of general Formula II



wherein R and X are as previously defined.

Preferably M is as previously defined for component (a). L may be a
compound according to Formula (VII) or (VIII) as previously defined. A
may be Cl, Br, I, NO₂, CuX₂ (where X is a halogen)

The invention also provides the use of the catalyst according to the first or

second aspect of the invention in the addition polymerisation of olefinically unsaturated monomers.

5 The components (a), (b) or (c), or (d) and (e) may be used together in any order.

Preferably the catalyst is used at a temperature of 20°C to 200°C.
preferably 50 to 130°C.

10 The olefinically unsaturated monomer may be methacrylate, acrylate, styrene, methacrylonitrile or a diene. Examples include:
C₁-C₄ methacrylic esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, sec-butyl methacrylate, isobutyl methacrylate and tert-butyl methacrylate, other
15 methacrylate esters such as cyclohexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, lauryl methacrylate.
Polyfunctional crosslinking agents such as glycidyl methacrylate and triethylene glycolmethacrylate, allyl methacrylate.

20 C₁-C₄ acrylic esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, isobutyl

acrylate and tert-butyl acrylate. other acrylate esters such as cyclohexyl acrylate, 2-ethylhexyl acrylate. octyl acrylate. decyl acrylate, lauryl acrylate. Polyfunctional crosslinking agents such as glycidyl acrylate and triethylene glycolacrylate. allyl acrylate.

5

Unsaturated nitriles such as methacrylonitrile and acrylonitrile. unsaturated imides such as optionally substituted maleimides aromatic vinyl compounds such as styrene, o-, m-, or p-methyl. ethyl. methoxy, chloro. nitro and styrene.

10

Aliphatic olefinic compounds such as butadiene and isoprene.

Preferably the co-catalysts are used in the ratios (c):(a) 0.01 to 1000, preferably 0.1 to 10. and (a):(b) 0.0001 to 1000, preferably 0.1 to 10.

15

where the degree of polymerisation is controlled by the ratio of monomer to (b).

The reaction may take place with or without the presence of a solvent.

Suitable solvents in which the catalyst. monomer and polymer product are sufficiently soluble for reactions to occur include propionitrile. hexane, heptane, dimethoxyethane. diethoxyethane. tetrahydroforan, ethylacetate.

20

diethylether, N,N-dimethylformamide, anisole, acetonitrile, toluene and xylene. Especially preferred solvents are xylene and toluene, preferably the solvents are used at at least 1% by weight, more preferably at least 10% by weight.

5

The reaction may be undertaken under an inert atmosphere such as nitrogen.

10

The reaction may be carried out in suspension, emulsion or in a dispersion.

Embodiments of the invention will now be described by way of example and with reference to the following figures:

15

Fig. 1 shows the structure of the ligand 2,6 dimethylanilineDAB:

Fig. 2 shows the crystal structure of the cation obtained by reacting tBuDAB and CuBr together;

Figs. 3 and 4 show Mn dependence on conversion of different monomer initiator ratios for styrene and methylmethacrylate respectively;

20

Fig. 5 shows Mw/Mn dependence on conversion for bulk polymerisation of styrene at 80°C;

Fig. 6 shows kinetic plots for polymerisation of methylmethacrylate at 90°C;

Fig. 7 shows the reaction scheme for the production of hydroxy terminally functionalised PMMA. (i) Br₂-P. (ii) Ethylene glycol. (iii) CuBr/3/MMA, (iv) benzoyl chloride:

Fig. 8 shows a selected region from ¹H NMR spectra of (a) 3, (b) 4 CH₂-O-groups and -OCH₃ \propto to Br and aromatic protons from benzoyl group;

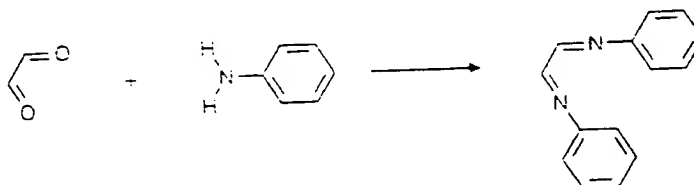
Fig. 9 shows partial MALDI-TOF-MS of 3 between x = 8 and 11. peaks correspond to lithium adducts of molecular ions with no observable fragmentation;

Fig. 10 shows a plot showing how Mn from SEC increases with conversion for experiments D-K.

Examples

Synthesis of Ligands

Diazabutadiene (DAB) Ligands



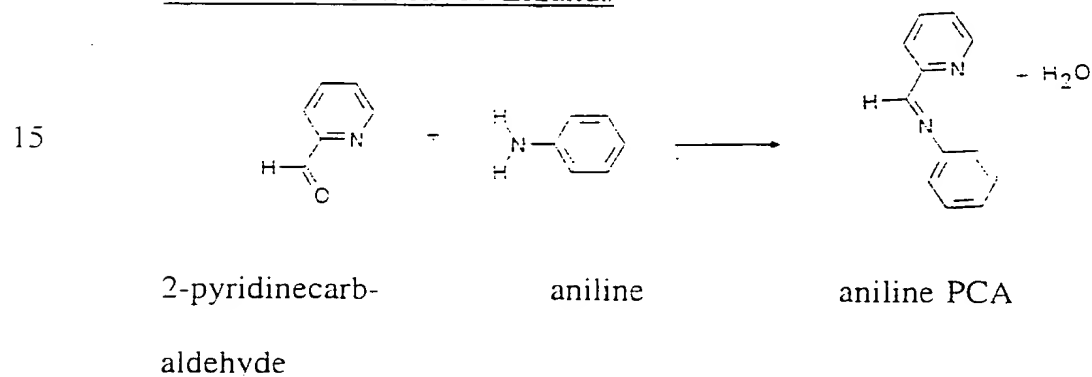
Glyoxal

Aniline

Dimethylaniline DAB

To a stirred solution of 40% aqueous glyoxal (0.25 mol) in a conical flask was added the required amine dropwise (0.5 mol). After a period of time a pale yellow solution formed which was taken up with water and filtered. The resulting precipitate was dissolved in diethyl ether and poured over a large excess of magnesium sulphate. The solution was left for twelve hours to remove all the water and the solution was filtered. Ether was removed on a rotary evaporator then the product recrystallised from ether. TertButyl DAB (tBu DAB) and isoPropyl DAB (iPr DAB) were similarly manufactured using t-butylamine and isopropylamine respectively as the starting amine. Such compounds are superior to 2.2-bipyridine in accepting electron density

Pyridine Carbaldehyde Ligands



20 To a stirred solution of pyridine carbaldehyde in ether was added an equimolar quantity of amine. The solution was left for 3 hours then

poured over an excess of magnesium sulphate. The solution was filtered and the ether removed on a rotary evaporator. Some ligands formed yellow oils and were purified by distillation under reduced pressure. Solids were purified by recrystallisation from ether.

5

tBu PCA, iPr PCA, nButyl PCA (nBu PCA), Dimethylaniline PCA, Diisopropylaniline PCA and methoxyaniline PCA were also made by reacting 2,6-dimethylaniline, 2,6-diisopropylaniline and 4-methoxyaniline, respectively as the amine.

Characterisation of Ligands

Ligands have been initially characterised by NMR and EI/CI mass spectrometry. Mass spec data is tabulated below.

DIAZABUTIENE (DAB) LIGANDS

| Structure | RMM | M/Z |
|---------------------|-----|-----|
| tBu DAB | 168 | 166 |
| iPr DAB | 140 | 141 |
| Dimethylaniline DAB | 262 | 249 |

PYRIDINE CARBALDEHYDE (PCA) LIGANDS

| Structure | RMM | M/Z |
|------------------------|-----|-----|
| tBu PCA | 162 | 163 |
| iPr PCA | 149 | 149 |
| nBu PCA | 162 | 163 |
| Aniline PCA | 182 | 182 |
| Dimethylaniline PCA | 212 | 209 |
| Diisopropylaniline PCA | 268 | 223 |
| Methoxyaniline PCA | 197 | 121 |

A crystal structure has been obtained of the ligand 2, 6 dimethylaniline DAB (Fig. 1). This shows a E configuration of double bonds which must fold around the metal centre to form the catalyst.

Synthesis of Catalysts

To a solution of ligand (in acetone) in a schlenk was added copper bromide , chloride or $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ under nitrogen. The solution was filtered by cannular and placed in a freezer. Solvent was removed by filtration and the crystals examined by FAB mass spectrometry. Catalysts were synthesised with equimolar quantities of ligand and anion or excess ligand (2:1). Both experiments resulted in the detection of a peak corresponding to CuL_2 .

L = ligand.

| Ligand | Ligand : anion | Anion | Mass spectrometry data M/Z | | | |
|--------|----------------|---------------|----------------------------|----------------|----------------------------------|------------------------------------|
| | | | CuL | CuL_2 | $\text{Cu}_2\text{L}_2\text{Cl}$ | $\text{Cu}_2\text{L}_2\text{Cl}_2$ |
| tBuDAB | 1:1 | Br | 231 | 399 | | |
| tBuDAB | 1:1 | BF_4 | 231 | 399 | | |
| tBuDAB | 2:1 | Br | 231 | 399 | | |
| tBuDAB | 1:1 | Cl | - | 399 | 499 | 597 |
| iPrDAB | 1:1 | Br | 203 | 343 | | |
| tBuPCA | 1:1 | Br | 225 | 387 | | |
| tBuPCA | 1:1 | BF_4 | 225 | 387 | | |
| tBuPCA | 1:1 | Cl | - | 387 | | |
| Bipy | 1:1 | Br | 300 | 456 | | |
| Bipy | 1:1 | BF_4 | 219 | 375 | | |
| Bipy | 2:1 | BF_4 | 219 | 375 | | |
| Bipy | 1:1 | Cl | - | 375 | | |

Bipy (Bipyridyl) is included as a comparison.

A crystal structure has been obtained for the reaction of tBu DAB and CuBr indicating a tetrahedral intermediate (Fig. 2).

Polymer Synthesis

The catalysts were used to control the propagation of styrene and methylmethacrylate. An effective catalyst should yield a polymer with a polydispersity of less than 1.5 and the M_n of the product increases with yield.

All polymerisations were performed with excess ligand 3:1 and the catalyst is synthesised in situ.

General method for polymerisation of methylmethacrylate

To a schlenk purged with nitrogen was added 0.54mls ethyl 2-bromo-isobutyrate (0.00372 mols) in 10mls methylmethacrylate (0.0935 mols).

The desired ligand was then added (0.01122 mols) and the entire solution freeze pump thaw degassed. 0.536g copper bromide (0.00374 mols) was then added whilst stirring. When the solution turned deep red indicating formulation of the catalyst the schlenk was immersed in an oil bath at 90°C.

Polymerisation results

All polymerisations are based on the following mole ratios.

Monomer : Initiator : Copper X : Ligand

100 : 1 : 1 : 3

Copper X = catalyst based on copper.

Styrene (Sty) was initiated with 1-phenylethyl bromide or chlorine.

Methylmethacrylate (MMA) was initiated with ethyl-2-bromo isobutyrate.

| ligand | mon. | X | t/hrs | T/°C | Mn | Mw | PDI | Conv% |
|---------------------|------|----|-------|------|--------|---------|------|-------|
| tBuDAB | STY | Br | 24 | 110 | 2.173 | 4.438 | 2 | 11 |
| iPrDAB | STY | Br | 24 | 110 | 1.975 | 72.587 | 38 | 5 |
| dimethylanilineDAB | STY | Br | 24 | 110 | 467 | 4.156 | 9 | 180 |
| tBuPCA | STY | Br | 24 | 110 | 338 | 1.110 | 3.2 | 1 |
| anilinePCA | STY | Br | 24 | 110 | 6.458 | 22.376 | 3.5 | 41 |
| dimethylaniline | STY | Br | 24 | 110 | 3.017 | 9.167 | 3 | 68 |
| tBuPCA | STY | Cl | 20 | 130 | 42.551 | 102.776 | 2.45 | 20 |
| nBuPCA | STY | Cl | 13 | 130 | 6.951 | 22.571 | 3.25 | 40 |
| iPrPCA | STY | Cl | 20 | 130 | 15.607 | 41.125 | 2.64 | 33 |
| anilinePCA | STY | Br | 20 | 110 | 6.458 | 22.376 | 4 | 41 |
| dimethylanilinePCA | STY | Br | 20 | 110 | 3.017 | 9.167 | 3 | 68 |
| isopropylanilinePCA | STY | Br | 20 | 130 | 3.700 | 10.074 | 2.72 | 61 |
| methoxyanilinePCA | STY | Br | 20 | 130 | 9.723 | 24.772 | 2.5 | 69 |
| anilinePCA | MMA | Br | 18 | 110 | 477 | 4.600 | 9.6 | 2 |
| dimethylanilinePCA | MMA | Br | 18 | 110 | 6.293 | 12.210 | 1.94 | 68 |
| nBuPCA | MMA | Br | 4 | 100 | 10.251 | 12.273 | 1.2 | 95 |
| nBuPCA | MMA | Br | 1 | 130 | 7.376 | 12.422 | 1.68 | - |
| nBuPCA | STY | Br | 40 | 80 | 5.492 | 7.313 | 1.33 | 43 |
| nBuPCA | STY | Br | 20 | 80 | 6.343 | 9.533 | 1.5 | 39 |

Polymerisation with tBuDAB

t-BuDAB was also investigated in more detail using different ratios of Ligand (L), Initiator (I) and catalyst (Cu).

5

Styrene at 100°C

| | <u>L:I</u> | <u>Cu:I</u> | <u>Mn</u> | <u>PDI</u> | <u>%Conv.</u> |
|----|------------|-------------|-----------|------------|---------------|
| | 3 | 1 | 2173 | 2.0 | 11 |
| 10 | 3 | 20 | 2603 | 4.0 | 7 |
| | 3 | 100 | 2169 | 5.8 | 8 |
| | 1 | 1 | 2400 | 3.6 | 9 |
| | 1 | 100 | 8042 | 14 | 7 |

15

MMA (100°C)

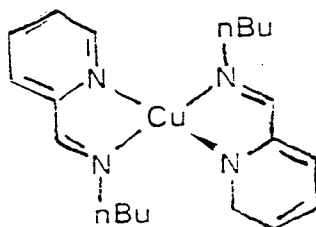
| | | | | |
|---|---|------|-----|-----|
| 3 | 1 | 2020 | 4.1 | Low |
|---|---|------|-----|-----|

This shows that PDI may be controlled by varying the ratio of L:I and/or Cu:I.

20

Polymerisations with nBuPCA

The most successful ligand was nBuPCA which will form the following copper (I) structure:



This catalyst has been used to obtain kinetic data for the polymerisation of both styrene and methylmethacrylate. Temperature control is important to prevent termination leading to tailing of the resulting MW distribution. If termination is prevented then polydispersity will decrease with time. Mn conversion plots have been obtained at different monomer to initiator ratios.

Figs. 3 and 4 show Mn dependence on conversion at different monomer:initiator for styrene and methylmethacrylate at 80°C.

Fig. 5 shows M_w/M_n dependence on conversion for bulk polymerisation of styrene at 80°C.

Fig. 6 shows kinetic plots for the polymerisation of methylmethacrylate at 90°C.

Synthesis of Block Co-polymers

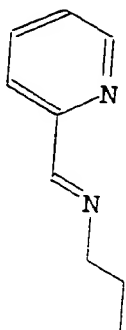
This was investigated using methylmethacrylate, benzylmethacrylate (BzMA) and 2 hydroxyethylmethacrylate (HEMA) the results of which are shown in the table below:

TABLE B

| BLOCK ONE | | | | BLOCK TWO | | | | |
|-----------|-------|-------|------|-----------|-------|--------|------|-------|
| Mon. | M_n | M_w | PDI | Mon. | M_n | M_w | PDI | % MMA |
| MMA | 2.469 | 2.965 | 1.2 | MMA | 5.599 | 7,337 | 1.31 | 100 |
| MMA | 2.469 | 2.965 | 1.2 | BzMA | 4.908 | 6,500 | 1.32 | 70 |
| MMA | 2.499 | 3.431 | 1.37 | BzMA | 5.934 | 10,749 | 1.81 | 54 |
| MMA | 2.499 | 3.431 | 1.37 | HEMA | 3.298 | 5,544 | 1.68 | 70 |

Further experimentation

Further experimentation was also carried out using ligands of Formula XII.



This was synthesised as follows:
30mls of diethylether was placed in a conical flask. 1.78mls of 2-pyridine
carbaldehyde (2.00g. 1.867×10^{-2} moles) were added prior to 1.54mls or
propylamine (1.11g. 1.873×10^{-2} moles). The reaction mixture
immediately turns yellow. The mixture was stored for 10 minutes at room
temperature prior to the addition of magnesium sulphate and stirring for a
further 30 minutes. The reaction mixture was filtered and the volatile
removed under reduced pressure. The product is isolated as a yellow oil.

Polymerisation

0.688g of copper (I) bromide (98% Aldrich)(4.796×10^{-3} moles) were
added to 10mls of methylmethacrylate (purified by passage down a

column containing basic alumina and 3A sieves under nitrogen (9.349×10^{-2} moles) in 20 mls of xylene (deoxygenated by 3 freeze-pump-thaw cycles and dried over 3A sieves for 12 hours). 0.2136g of A (1.44×10^{-3} moles) were added over 2 minutes with stirring at room temperature to give a homogenous deep red/brown solution. 0.07mls of ethyl 2-bromoisobutyrate (0.0924g, 4.73×10^{-4} moles) were added and the reaction mixture heated to 90°C for 485 minutes. Samples were taken at intervals and analysed for Mn and conversion. see table. After 485 minutes poly(methylmethacrylate) was isolated by precipitation into methanol in 78.6% yield with Mn = 7020 and PDI (M_w/M_n) = 1.27.

| <u>TIME</u> | <u>% CONVERSION</u> | <u>Mn</u> | <u>PDI</u> |
|-------------|---------------------|-----------|------------|
| 120 | 16.47 | 2376 | 1.28 |
| 240 | 52.69 | 5249 | 1.22 |
| 300 | 61.02 | 6232 | 1.18 |
| 360 | 67.56 | 6742 | 1.21 |
| 485 | 78.56 | 7020 | 1.27 |

The Production of α -hydroxy terminally functionalised PMMA

The initiator, ethyl-2-bromoisobutyrate was replaced with hydroxy

containing alkyl bromide so as to produce α -hydroxy terminally functionalised PMMA without the need to employ protecting group chemistry.

5 Ligands of Formula XII were used in the polymerisation process.

2-hydroxyethyl-2'-methyl-2'-bromopropionate was prepared as shown in Fig. 7.

10 The conditions used in steps (1) and (ii) was as follows:
0.25g of red phosphorous (8.06×10^{-3} mol) were added to 35.4ml (0.338 mol) of isobutyryl chloride. The mixture was placed under gentle reflux and 20ml of bromine (0.338 mol) were added slowly over 8 hours. The mixture was refluxed for a further 4 hours and the crude reaction mixture
15 added slowly to 350ml of anhydrous ethylene glycol (6.27 mol). The reaction mixture was refluxed for 4 hours, filtered into 500ml of distilled water and the product extracted into chloroform. After washing with water and sodium hydrogen carbonate and drying over magnesium sulfate the product was isolated as a colourless liquid after the removal of solvent
20 and vacuum distillation at 64.5°C and 0.1 Torr. ^1H NMR (CDCl_3 , 373 K. 250.13 MHz) δ = 4.30 (t, J 9.6 Hz, 2H). 3.85 (t, J 9.6 Hz, 2H) 1.94 s,

6H), ^{13}C (^1H) NMR (CDCl_3 , 373 K, 100.6 MHz) δ = 171.83, 67.30, 60.70, 55.72, 30.59, IR (NaCl. film) 3436 (br), 2977, 1736 (s), 1464, 1391, 1372, 1278, 1168, 1112, 1080, 1023, 950, 644, EI MS: 213, 211 (mass peaks), 169, 167, 151, 149, 123, 121. The typical polymerisation procedure used

(steps iii and iv) was as follows:

0.1376 of copper(I)bromide (98%, 9.6×10^{-4} mol) were added to 40ml of xylene and 20ml of methyl methacrylate (0.187 mol). 0.4272g of 2 (2.89×10^{-3} mol) were added and the mixture deoxygenated by one freeze-pump-thaw cycle prior to the addition of 0.2029g of 3 (9.61×10^{-4}) mol at room temperature. The deep red solution was heated at 90°C for 70 minutes. The final product was isolated by precipitation into hexanes.

Atom transfer radical polymerisation of MMA using 3 as initiator in conjunction with 2 and CuBr was carried out at 90°C in xylene

[MMA]:[3] = 20:1, [ligand]:[CuBr]:[3] = 3:1:1 to give PMMA of structure

4. Polymerisation was stopped at low conversion, 7.65%, after 70 minutes, so as to reduce the amount of termination by radical-radical reactions, reaction A. ^1H NMR data (Fig. 8), clearly shows the presence of the hydroxyethyl ester group, originating from 2 and the methoxy \propto to the bromo group at the propagating end at δ 4.28, 3.82 and 3.74 respectively. The number average molecular mass, M_n , can be calculated

directly from NMR which gives a value of 2430 which compares excellently with that obtained from size exclusion chromatography against PMMA standards of 2320, PDI = 1.12 (when precipitated into hexanes M_n - 2960, PDI = 1.12). This excellent agreement indicates that the product

5 has structure 4. This is confirmed by matrix-assisted laser desorption-ionisation time of flight mass spectrometry, Fig. 9. We see one series of peaks in the MALDI-TOF-MS indicating only one predominant structure i.e. 4. For example, the peaks at m/z 1319.0 and 1419.2 correspond to lithium adducts of 4 where $x = 10$ and 11 respectively. calculated m/z

10 1318.3 and 1418.4. The narrow PDI of 4 is indicative of $k(\text{propagation}) > k(\text{termination})$ i.e. pseudo living polymerisation. Control over M_n and PDI is obviously not affected detrimentally by the presence of primary alcohol group present in the initiator, which might have been expected to complicate the reaction by coordination to the copper catalyst. Indeed the

15 PDI is narrower and the rate of polymerisation faster with 3 than that obtained using a non functional initiator. This is currently under investigation. Thus ATRP with the copper complex as catalyst can be utilised to give PMMA or structure 4 as the only detectable product under these conditions. The hydroxy group can be further reacted with benzoyl

20 chloride to give 5 quantitatively.

relative to propagation. ¹²

In summary atom transfer radical polymerisation with the copper complex as catalyst and 3 as initiator leads to α -hydroxy functional PMMA. The presence of the hydroxy group during the polymerisation does not reduce the control over the polymerisation, and a narrow PDI polymer with controlled Mn is obtained. The reaction shows all the characteristics of a living/pseudo living polymerisation. The structure of the product has been confirmed by MALDI-TOF-MS and NMR spectrometry. Furthermore the hydroxy functionality can be further functionalised by reaction with acid chlorides in a quantitative reaction.

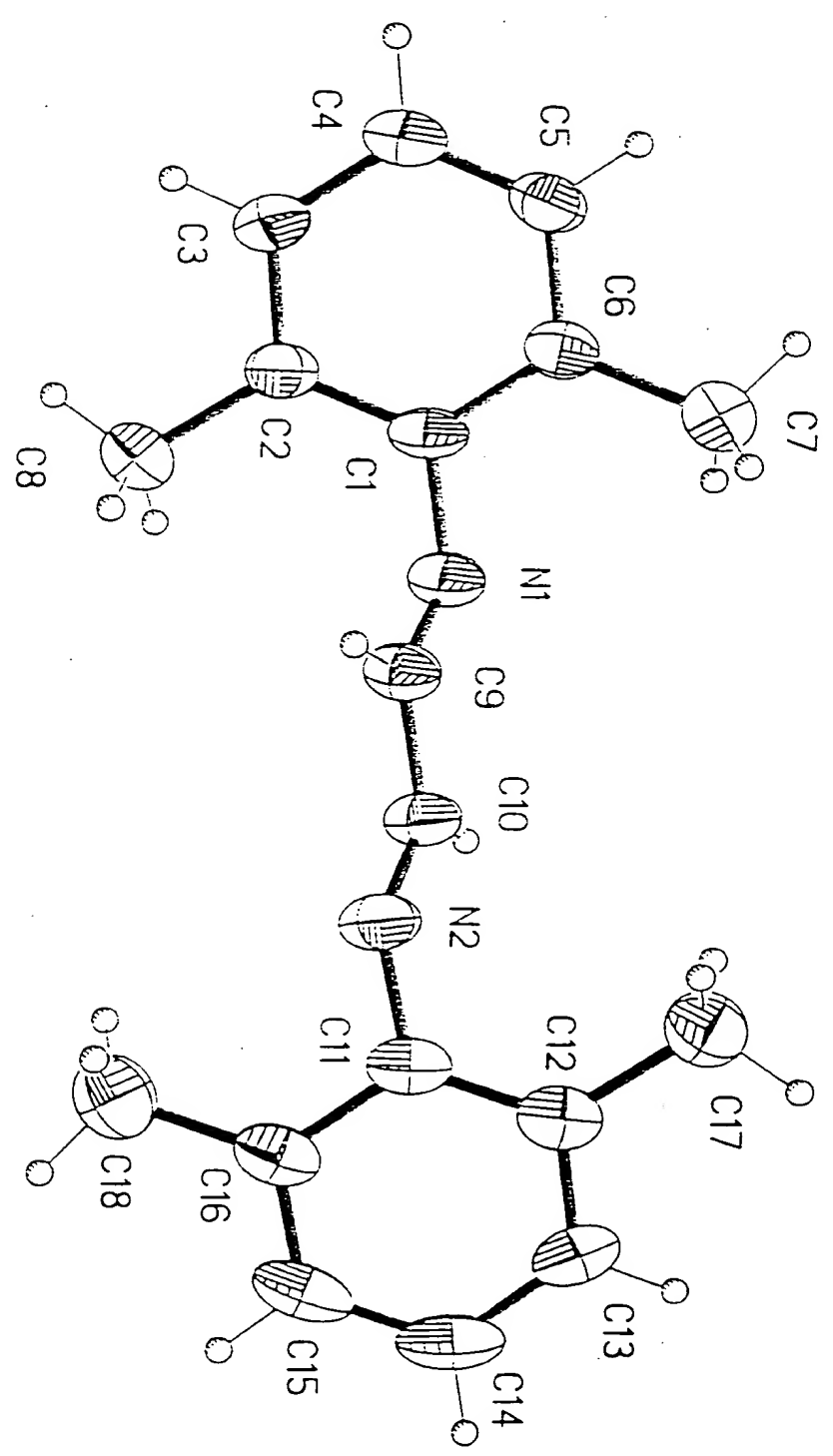
| Reaction ^a | [3]/ 10 ⁻² mol | [MMA]/ mol | t/min | Conversion (%) ^d | Mn SEC | PDI SEC |
|-----------------------|------------------------------|---------------|-------|--------------------------------|---------------------|-------------------|
| A ^b | 9.61 | 0.187 | 70 | — | 2530 | 1.10 |
| B ^c | 9.72 | 0.047 | 120 | — | 4540 ^c | 1.22 ^c |
| C ^c | 9.72 | 0.047 | 120 | — | 3130 | 1.22 |
| D ^b | 9.61 | 0.187 | 60 | 0.21 | — | — |
| E ^b | 9.61 | 0.187 | 120 | 2.27 | — | — |
| F ^b | 9.61 | 0.187 | 180 | 15.74 | 4980 | 1.21 |
| G ^b | 9.61 | 0.187 | 240 | 48.20 | 12 330 | 1.26 |
| H ^b | 9.61 | 0.187 | 300 | 59.75 | 15 580 | 1.29 |
| I ^b | 9.61 | 0.187 | 360 | 66.18 | 17 920 | 1.27 |
| J ^b | 9.61 | 0.187 | 420 | 72.11 | 19 500 | 1.27 |
| K ^b | 9.61 | 0.187 | 480 | 75.05 | 20 100 | 1.28 |
| L ^b | 9.61 | 0.187 | 480 | — | 19 427 ^c | 1.31 ^c |

^a All reactions carried out with [2]:[CuBr]:[3] = 3:1:1. ^b 20 ml MMA in 40 ml xylene. ^c 5 mls MMA in 6 ml xylene. ^d From gravimetry. ^e After precipitation, otherwise as taken from reaction flask.

The terminal benzoyl group of 5 is observed by ^1H NMR, Fig. 8(c) and is detected by SEC with UV detection at 200 nm. 4 shows no absorption at this wavelength. MALDI TOF shows a new series of peaks corresponding to 5 e.g. peaks are now observed at m/z 1423.0 and 1522.8 for $x = 10$ and 11, calculated m/z 1422.3 and 1522.4; this reaction is quantitative and no peaks from residual 4 are observed. When the reaction is carried out at a higher $[\text{MMA}]:[3]$ ratio for 120 minutes a higher molecular weight polymer is produced. $M_n = 4540$, $PDI = 1.22$, as expected, reactions B and C. Again analysis shows terminal hydroxy functionally.

Living or pseudo living polymerisations have a low rate of termination relative to rate of propagation. This is demonstrated by following a reaction with time, reactions D-K: L is the final product from this reaction. Fig. 10 shows that M_n increases linearly with conversion, up to approx. 80%, whilst PDI remains narrow for reaction with $[\text{MMA}]:[3] = 200$. In this case the expected M_n (theory) at 100% conversion = $[100/1 \times 100.14 \text{ (mass of MMA)}] + 220 \text{ (mass of end groups)} = 20248$. The PDI is broader than would be expected for a true living polymerisation with fast initiation (theoretically $1 + 1/DP$). However, PDI does not increase with increasing conversion as would be expected for a reaction with significant termination and this is most probably due to slow initiation

Figure 1



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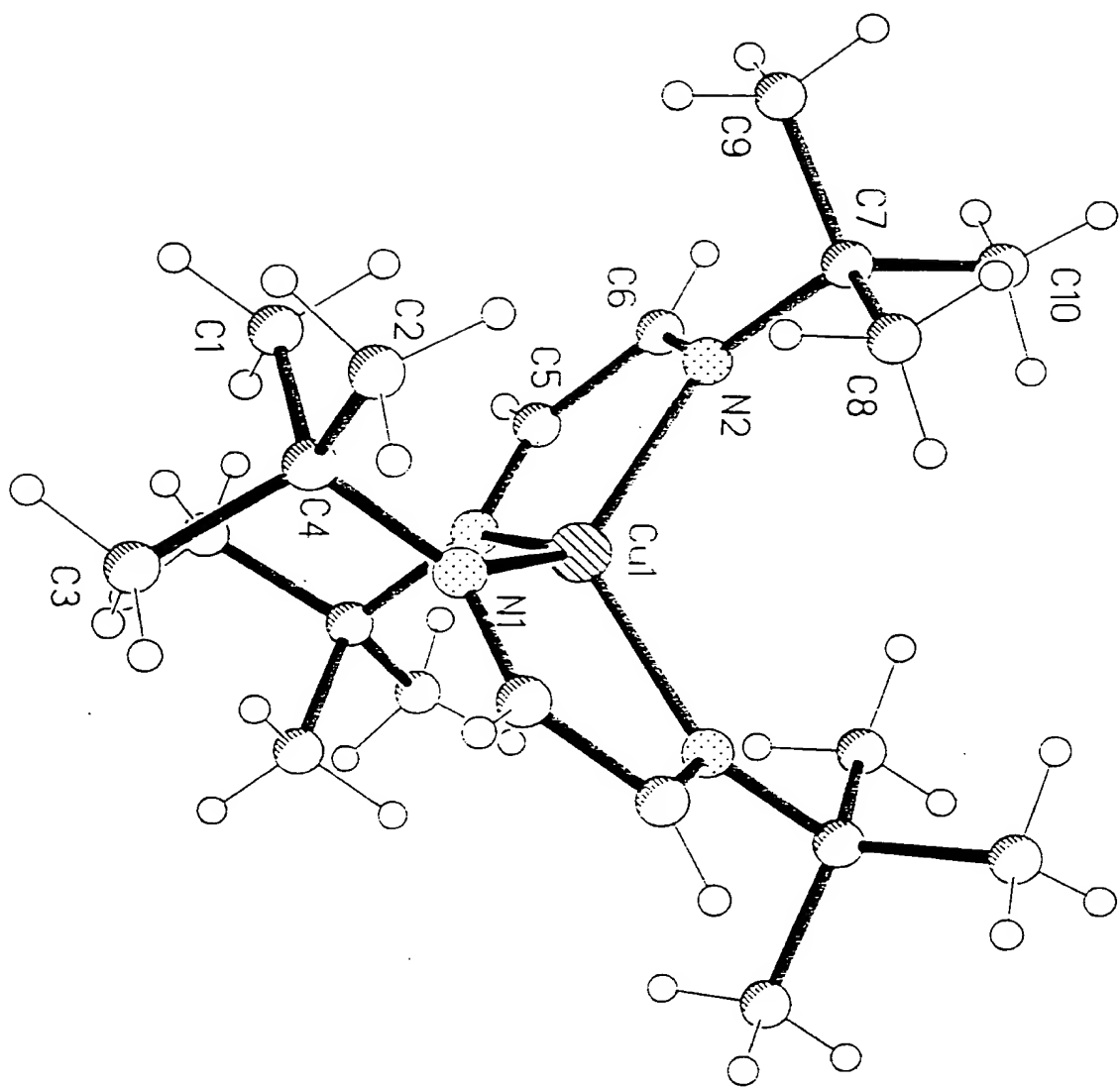


Figure 2

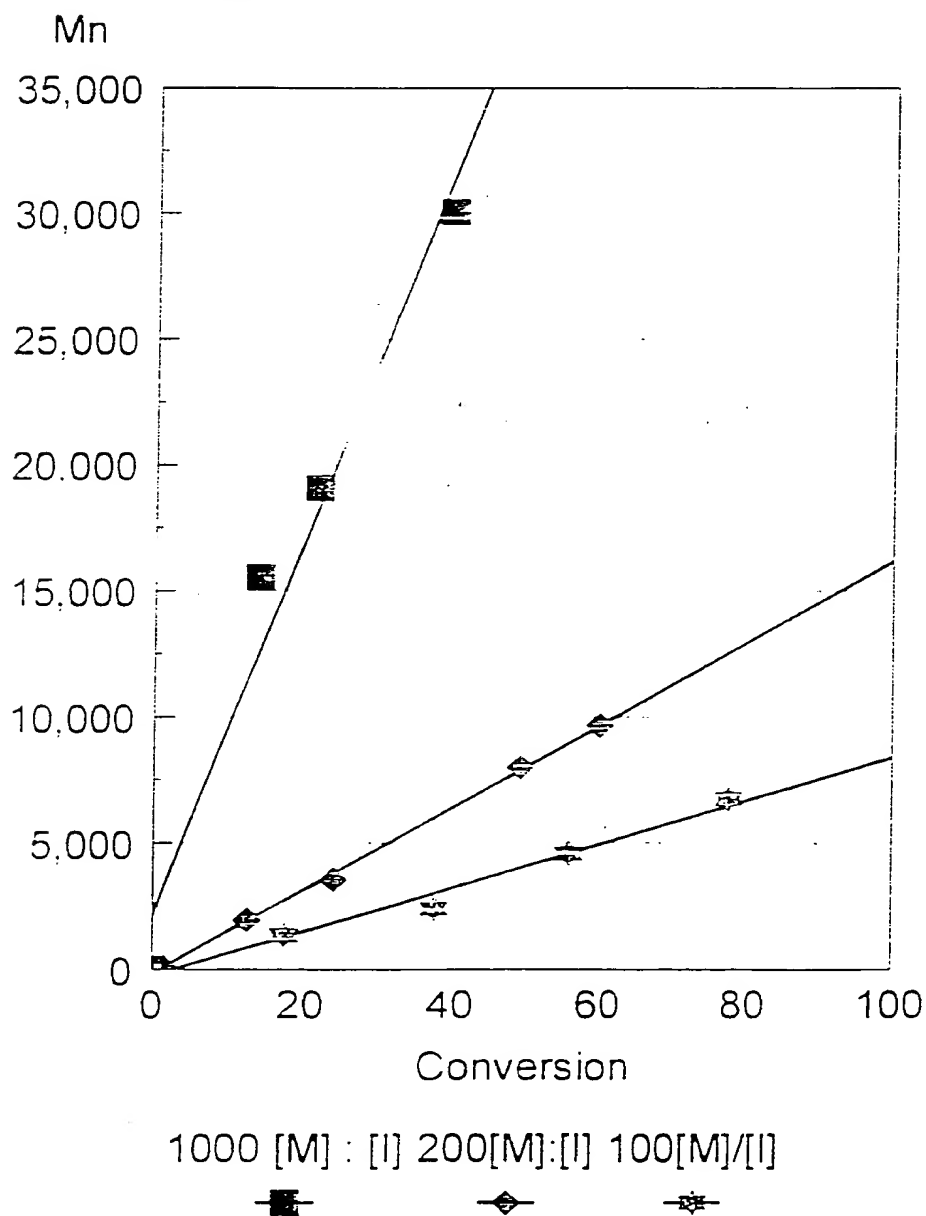
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Figure 3

Mn dependance on conversion

at different monomer: Initiator ratios

Polymerisation of styrene at 80C

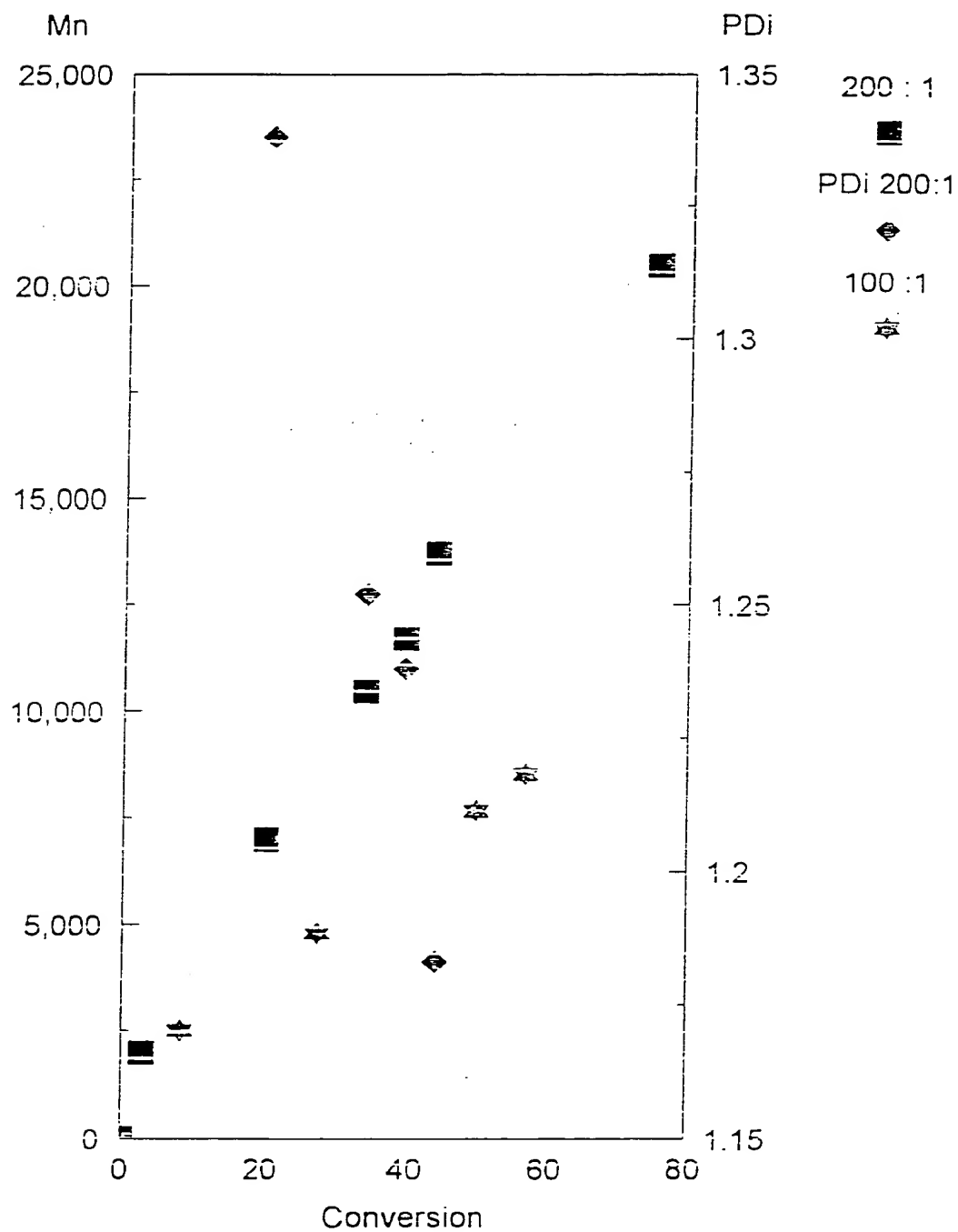


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Fig. 4.

Mn dependance on Conversion

at different MMA : Initiator ratios



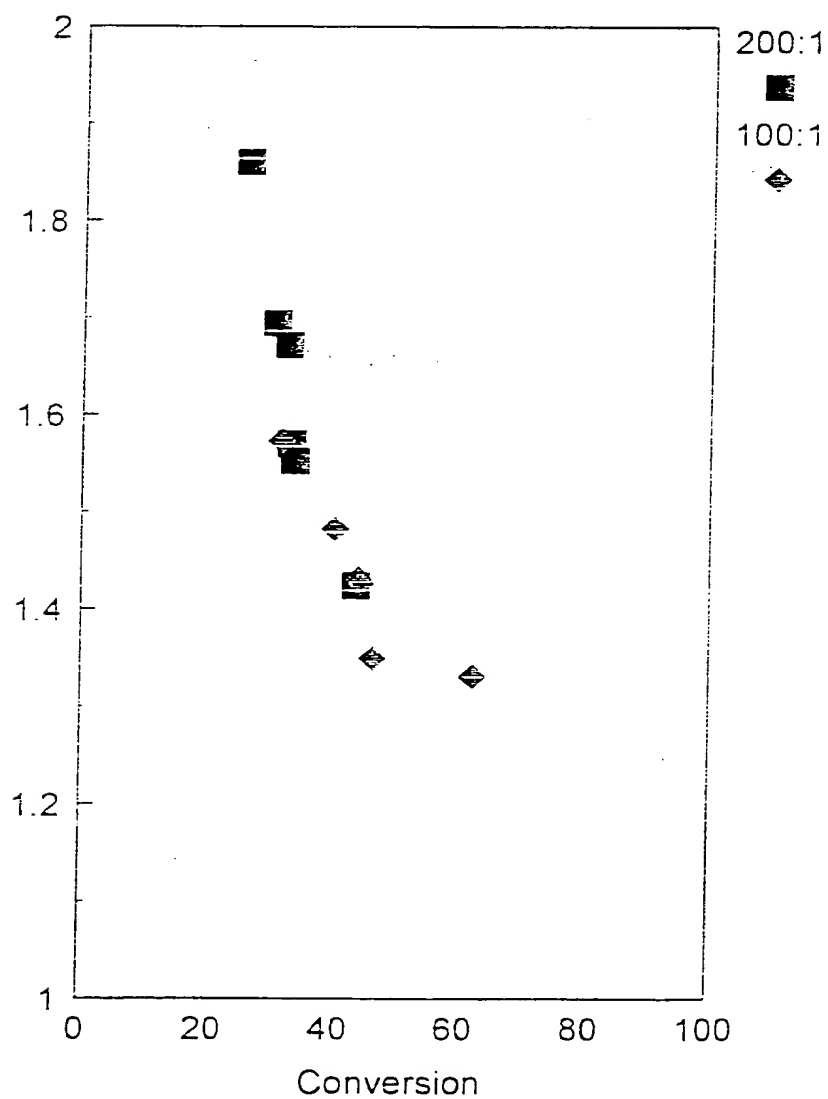
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Figure 5

Mw/Mn dependance on conversion

Bulk polymerisation of styrene at 80C

Mw/Mn

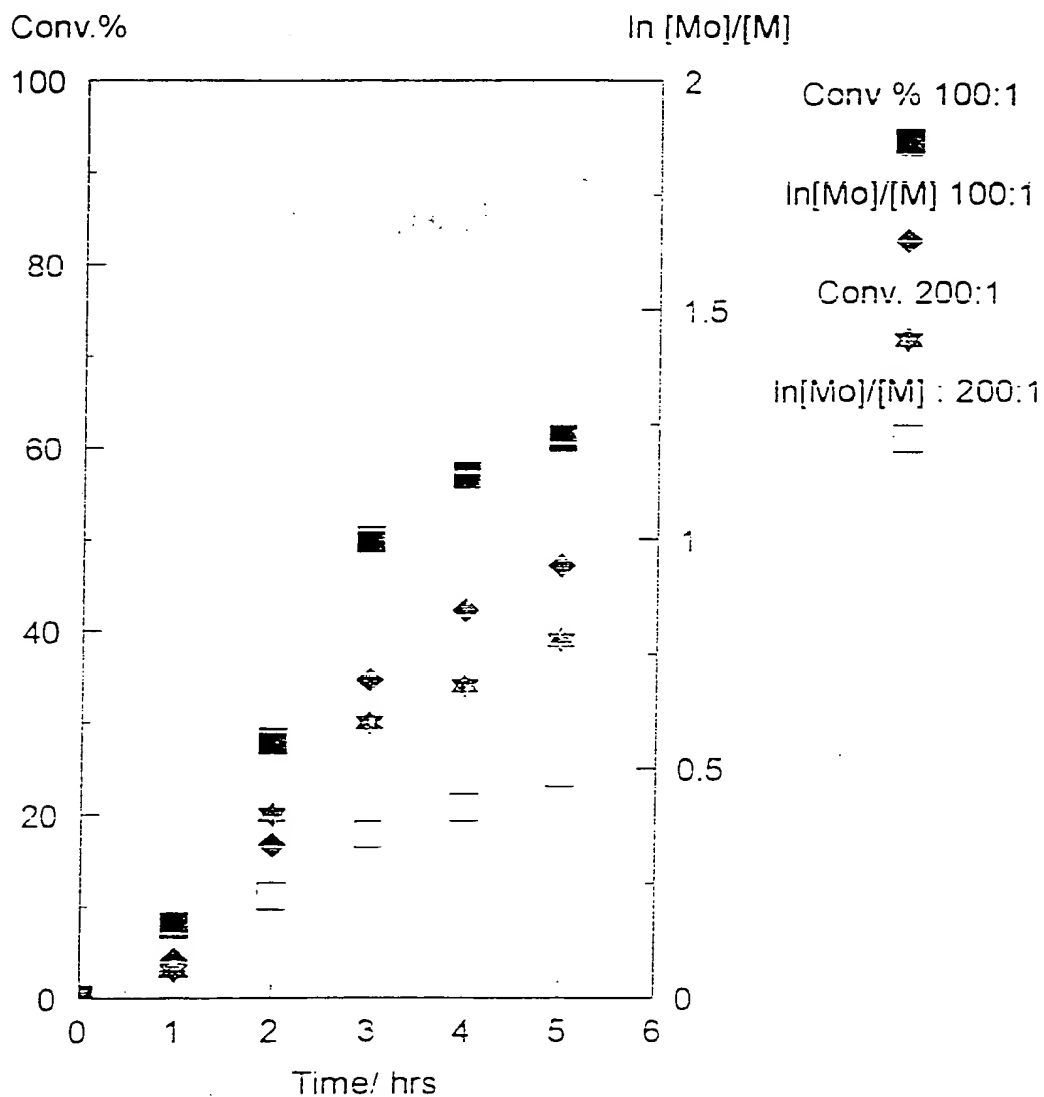


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Figure 6

KINETIC PLOTS FOR THE POLYMERISATION OF MMA

POLYMERISATION AT 90°C
at two monomer to initiator ratios



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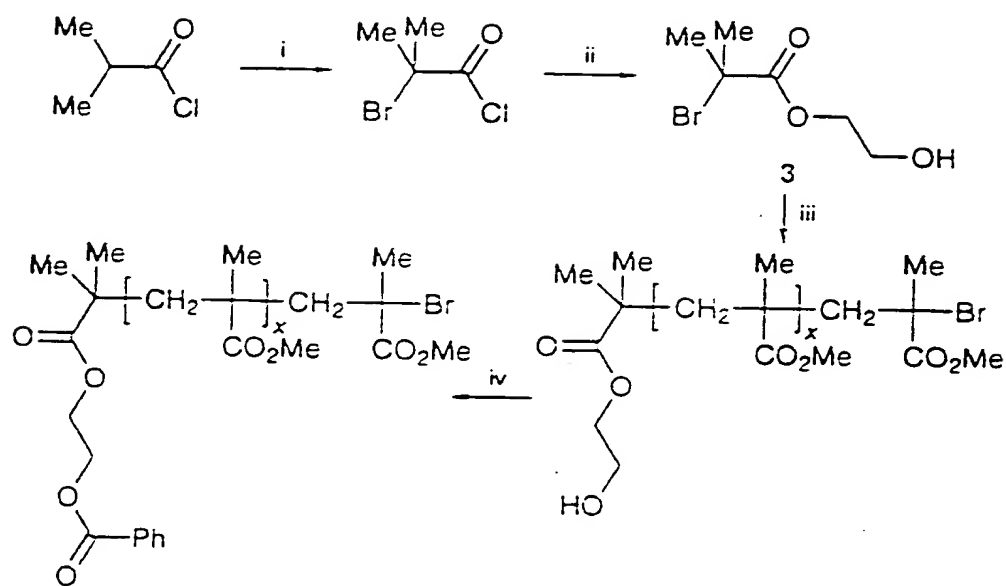


FIGURE 7

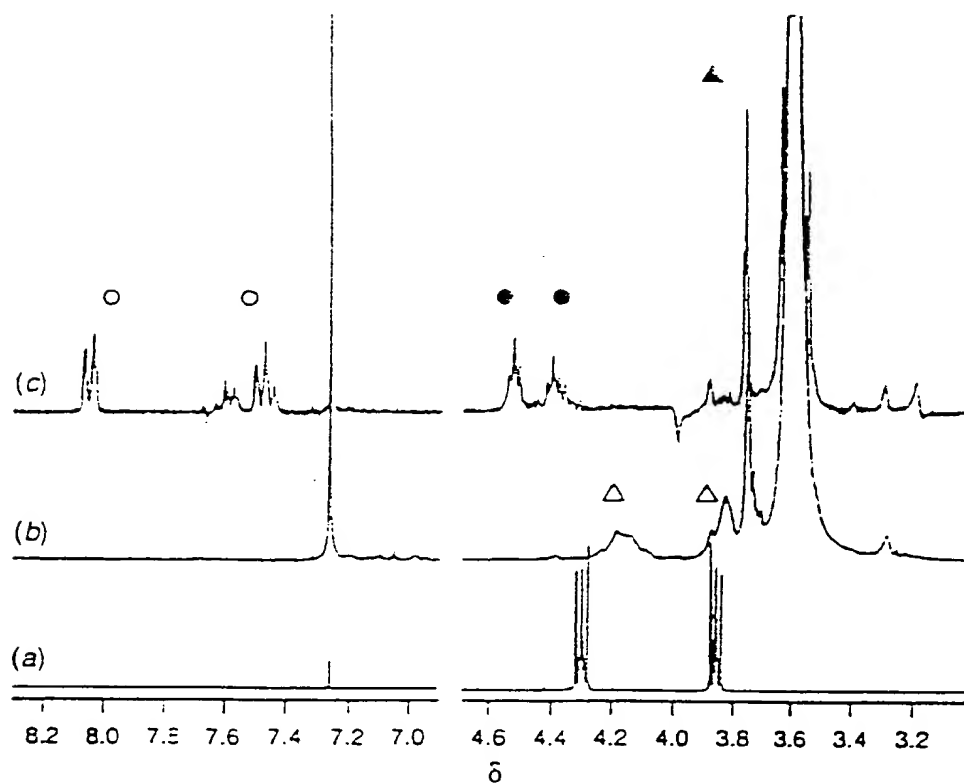


FIGURE 8

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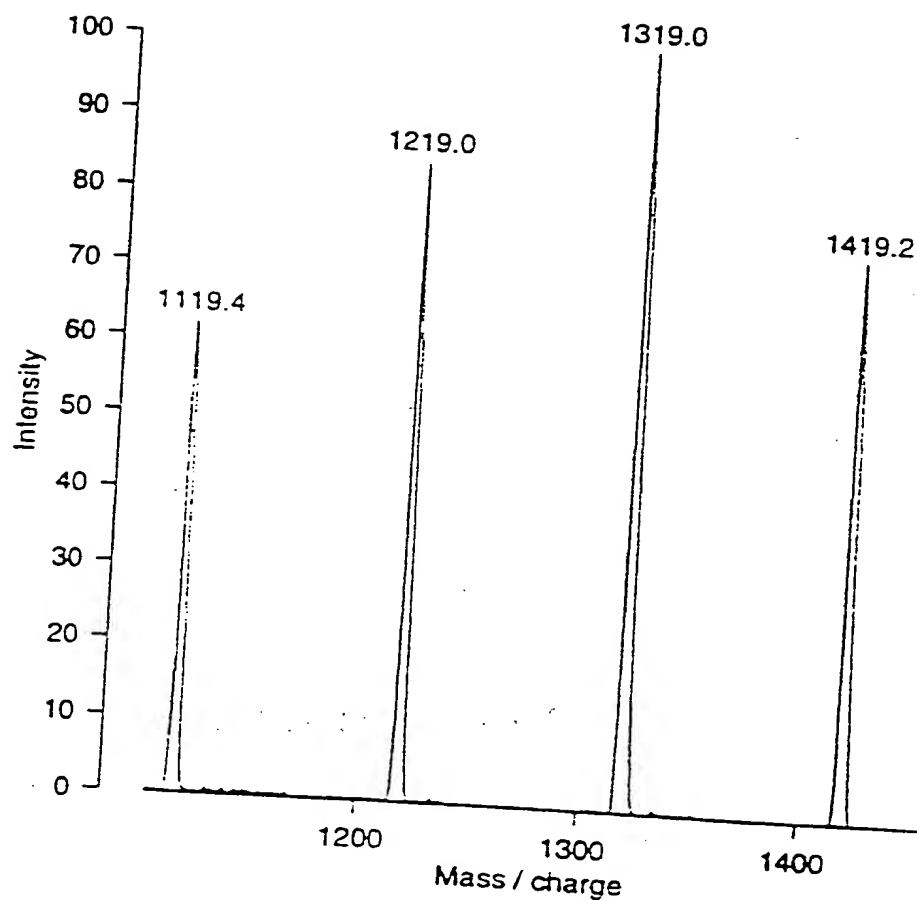


FIGURE 9

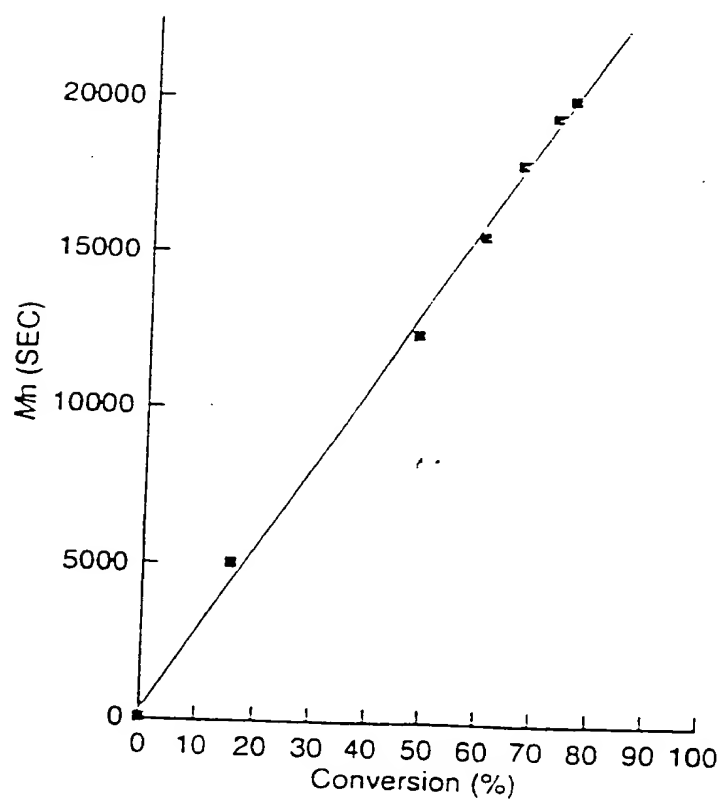


FIGURE 10

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Number of earlier application

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POLYMERISATION CATALYST AND PROCESS

The present invention relates to a process for the free radical initiated polymerisation of olefinically unsaturated monomers in which molecular weight control is achieved by the presence of certain transition metal, especially copper, diimine complexes. These copper complexes can be formed with either by reaction of copper(I) salts with appropriate diimines in situ or the isolated copper-diimine complex may be used. Copper(I) diimine complexes are used in conjunction with an appropriate alkyl halide.

It is desirable to be able to produce high molecular weight polymers with a low molecular weight distribution by catalysed addition polymerisation by a free radical process, in particular of vinylic monomers. Hitherto this has been achieved by polymerising via ionic processes typically in the presence of organometallics such as alkyl lithium's which are sensitive as regards reaction with water and other protic species. As such monomers containing functional groups are not readily polymerised. The use of ionic systems also precludes the use of solvents which contain protic groups and/or impurities resulting in very stringent reaction conditions and reagent purity being employed.

More recently systems based on the combination of a transition metal halide and alkyl halide have been utilised. For example Matyjasewski (Macromolecules (1995), vol 28, pages 7901-7910) has described the use of CuX (where X=Cl, Br) in conjunction with bipyridine and an alkyl halide to give polymers of narrow molecular weight distribution and controlled molecular weight. This system suffers from the disadvantage that the copper catalyst is only partially soluble in the system and thus a heterogeneous polymerisation ensues. The level of catalyst which is active in solution is thus difficult to determine. Precec Macromolecules, (1995), vol. 28, page 1995) has extended Matyjasewski's work by utilising arenesulphonyl chlorides to replace alkyl chlorides, again this results in heterogeneous polymerisation. Sawamoto (Macromolecules, (1995), vol. 28, page 1721) has also utilised a ruthenium based system for similar polymerisation of methacrylates. This system requires activation of monomer by aluminium alkyl, itself sensitive to reaction with protic species which is an inherent disadvantage.

Surprisingly the inventors have found that the use of diimines such as 1,4-diaza-1,3-butadienes and 2-pyridinecarbaldehyde imines may be used in place of bipyridines. These ligands offer the advantage of

homogeneous polymerisation and thus the level of active catalyst can be accurately controlled. This class of ligand also enables the control of the relative stability of the transition method valencies, for example, Cu(I) and Cu(II), by altering ancillary substituents and thus gives control over the nature of the products through control over the appropriate chemical equilibrium. Such a system is tolerant to trace impurities, trace levels of O₂ and monofunctional monomers, and may be conducted in aqueous media.

Accordingly a first aspect of the invention provides a catalyst for addition polymerisation of olefinically unsaturated monomers, especially vinylic monomers, comprising:

a) a first compound of formula I



where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and X is a monovalent anion;

b) a second compound of general formula II



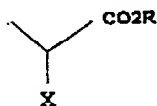
where R = alkyl C_nH_{2n+1}, where n is a whole number, benzyl PhCH₂, or substituted benzyl and x = Cl, Br, I; and

c) an organodiimine.

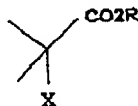
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Transitional metals may have different valencies, for example Fe(II) and Fe(III), Cu(I) and Cu(II), a low valency state is the lower of the commonly occurring valencies, i.e. Fe(II) or Cu(I). Hence M in Formula I is preferably Cu(I), Fe(II), Co(II), Ru(II) or Ni(II), most preferably Cu(I). Preferably the co-ordinating ligand is Cu(CH₃CN)₄. X may be chosen from Cl, Br, I, NO₂, PF₆, or BF₄.

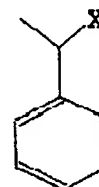
10 Preferably the second component (b) is selected from



Formula III

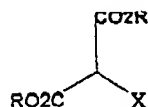


Formula IV



Formula V

or

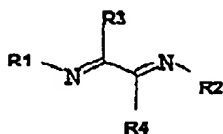


Formula VI

where R is as defined previously.

25 Component (c) may be selected from 1,4-diaza-1,3-butadiene

5

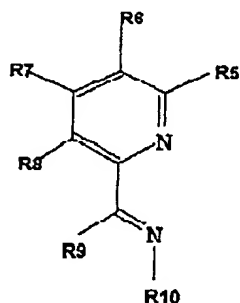


5

Formula VII

or a 2-pyridinecarbaldehyde imine

10



Formula VIII

15

where R_1 , R_2 and R_{10} may be varied independently and R_1 , R_2 and R_{10} may be H, straight chain or branched chain saturated alkyl, aryl (such as phenyl or phenyl substituted where substitution is as described for R_1 to R_9), CH_2Ar (where Ar = aryl) or a halogen.

20

Preferably R_1 , R_2 and R_{10} may be a C_1 to C_{10} alkyl, in particular C_1 to C_6 alkyl, methacrylate, ethylmethacrylate, n-propylisopropyl, n-butyl, sec-butyl, tert butyl, cyclohexyl, 2-ethylhexyl, octyl decyl or lauryl. R_1 , R_2 and R_{10} may especially be methyl.

25

R_1 to R_9 may independently be selected from the group described for R_1 , R_2 and R_{10} or additionally OCH_3 .

6

(where n is an integer from 1 to 20), NO₂, CN or O=CR
(where R = alkyl, benzyl PhCH₂, or a substituted
benzyl).

5 Compounds of general Formula VIII may comprise one or
more fused rings on the pyridine group.

Adjacent R₁ and R₂, R₃ and R₄, R₅ and R₆, R₇ and R₈, R₉
and R₁₀, R₁₁ and R₁₂, R₁₃ and R₁₄, R₁₅ and R₁₆ groups may be C₁
10 to C₆ cycloalkyl, C₁ to C₆ cycloalkenyl,
polycycloalkyl, polycycloalkenyl or cyclicaryl, such
as cyclohexyl, cyclohexenyl or norborneyl.

A second aspect of the invention provides a catalyst
15 for addition polymerisation of olefinically
unsaturated monomers, especially vinylic monomers,
comprising:

a first component of Formula XI

20 [ML₂]⁺A⁻

wherein M = a transitional metal in a low valency
state;

L = an organodiimine

A = a monovalent anion.

25

(e) A second component of general Formula II

RX

7

wherein R and X are as previously defined.

Preferably M is as previously defined for component
(a). L may be a compound according to Formula (VII)
5 or (VIII) as previously defined. A may be Cl, Br, I,
NO₂, CuX, (where X is a halogen)

The invention also provides the use of the catalyst
according to the first or second aspect of the
10 invention in the addition polymerisation of
olefinically unsaturated monomers.

The components (a), (b) or (c), or (d) and (e) may be
used together in any order.

15 Preferably the catalyst is used at a temperature of
20°C to 200°C, preferably 50 to 130°C.

The olefinically unsaturated monomer may be
20 methacrylate, acrylate, styrene, methacrylonitrile or
a diene. Examples include:

C₁₋₄ methacrylic esters such as methyl methacrylate,
ethyl methacrylate, n-propyl methacrylate, isopropyl
methacrylate, n-butyl methacrylate, sec-butyl
25 methacrylate, isobutyl methacrylate and tert-butyl
methacrylate, other methacrylate esters such as
cyclohexyl methacrylate, 2-ethylhexyl methacrylate,

8

octyl methacrylate, decyl methacrylate, lauryl methacrylate. Polyfunctional crosslinking agents such as glycidyl methacrylate and triethylene glycolmethacrylate, allyl methacrylate.

5

C₁₋₄ acrylic esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, isobutyl acrylate and tert-butyl acrylate, other acrylate esters such as cyclohexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, decyl acrylate, lauryl acrylate. Polyfunctional crosslinking agents such as glycidyl acrylate and triethylene glycolacrylate, allyl acrylate.

10

15

Unsaturated nitriles such as methacrylonitrile and acrylonitrile, unsaturated imides such as optionally substituted maleimides aromatic vinyl compounds such as styrene, o-, m-, or p-methyl, ethyl, methoxy, chloro, nitro and styrene.

20

Aliphatic olefinic compounds such as butadiene and isoprene.

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Preferably the co-catalysts are used in the ratios (c):(a) 0.01 to 1000, preferably 0.1 to 10, and (a):(b) 0.0001 to 1000, preferably 0.1 to 10, where

the degree of polymerisation is controlled by the ratio of monomer to (b).

5 The reaction may take place with or without the presence of a solvent. Suitable solvents in which the catalyst, monomer and polymer product are sufficiently soluble for reactions to occur include propionitrile, hexane, heptane, dimethoxyethane, diethoxyethane, tetrahydroforan, ethylacetate, diethylether, N,N-
10 dimethylformamide, anisole, acetonitrile, toluene and xylene. Especially preferred solvents are xylene and toluene, preferably the solvents are used at at least 1% by weight, more preferably at least 10% by weight.

15 The reaction may be undertaken under an inert atmosphere such as nitrogen.

The reaction may be carried out in suspension, emulsion or in a dispersion.

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Embodiments of the invention will now be described by way of example and with reference to the following figures:

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Fig. 1 shows the structure of the ligand 2,6 dimethylanilineDAB;

Fig. 2 shows the crystal structure of the cation

10

obtained by reacting tBuDAB and CuBr together;

Figs. 3 and 4 show Mn dependence on conversion of different monomer initiator ratios for styrene and methylmethacrylate respectively;

5 Fig. 5 shows Mw/Mn dependence on conversion for bulk polymerisation of styrene at 80°C; and,

Fig. 6 shows kinetic plots for polymerisation of methylmethacrylate at 90°C.

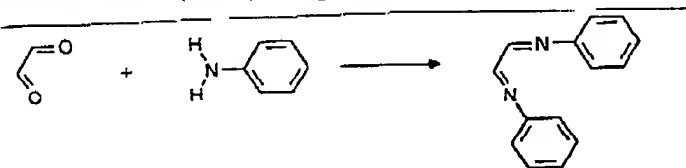
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Examples

Synthesis of Ligands

Diazabutadiene (DAB) Ligands

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Glyoxal

Aniline

Dimethylaniline DAB

(phenylamine)

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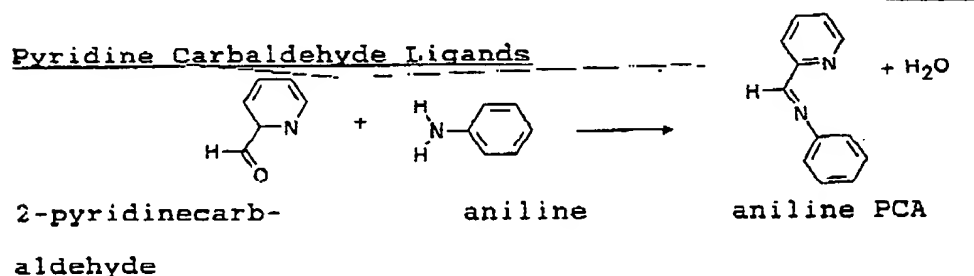
To a stirred solution of 40% aqueous glyoxal (0.25 mol) in a conical flask was added the required amine dropwise (0.5 mol). After a period of time a pale yellow solution formed which was taken up with water and filtered. The resulting precipitate was dissolved in diethyl ether and poured over a large excess of magnesium sulphate. The solution was left for twelve hours to remove all the water and the solution was filtered. Ether was removed on a rotary evaporator

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11

then the product recrystallised from ether. TertButyl DAB (tBu DAB) and isoPropyl DAB (iPr DAB) were similarly manufactured using t-butylamine and isopropylamine respectively as the starting amine. Such compounds are superior to 2,2-bipyridine in accepting electron density

10



15

To a stirred solution of pyridine carbaldehyde in ether was added an equimolar quantity of amine. The solution was left for 3 hours then poured over an excess of magnesium sulphate. The solution was filtered and the ether removed on a rotary evaporator. Some ligands formed yellow oils and were purified by distillation under reduced pressure. Solids were purified by recrystallisation from ether.

20

tBu PCA, iPr PCA, nButyl PCA (nBu PCA),

25

Dimethylaniline PCA, Diisopropylaniline PCA and methoxyaniline PCA were also made by reacting 2,6-dimethylaniline, 2,6-diisopropylaniline and 4-methoxyaniline, respectively as the amine.

CHARACTERISATION OF LIGANDS

Ligands have been initially characterised by NMR and EI/CI mass spectrometry. Mass spec data is tabulated below.

DIAZABUTDIENE (DAB) LIGANDS

| Structure | RMM | M/Z |
|---------------------|-----|-----|
| tBu DAB | 168 | 166 |
| iPr DAB | 140 | 141 |
| Dimethylaniline DAB | 262 | 249 |

PYRIDINE CARBALDEHYDE (PCA) LIGANDS

| Structure | RMM | M/Z |
|------------------------|-----|-----|
| tBu PCA | 162 | 163 |
| iPr PCA | 149 | 149 |
| nBu PCA | 162 | 163 |
| Aniline PCA | 182 | 182 |
| Dimethylaniline PCA | 212 | 209 |
| Diisopropylaniline PCA | 268 | 223 |
| Methoxyaniline PCA | 197 | 211 |

A crystal structure has been obtained of the ligand 2, 6 dimethylaniline DAB (Fig. 1). This shows a E configuration of double bonds which must fold around the metal centre to form the catalyst.

SYNTHESIS OF CATALYSTS

To a solution of ligand (in acetone) in a schlenk was added copper bromide , chloride or $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ under nitrogen. The solution was filtered by cannular and placed in a freezer. Solvent was removed by filtration and the crystals examined by FAB mass spectrometry. Catalysts were synthesised with equimolar quantities of ligand and anion or excess ligand (2:1). Both experiments resulted in the detection of a peak corresponding to CuL_2 .

L = ligand.

| Ligand | Ligand : anion | Anion | Mass spectrometry data M/Z | | | |
|--------|----------------|-----------------|----------------------------|------------------|-----------------------------------|--|
| | | | CuL | CuL ₂ | Cu ₂ L ₂ Cl | Cu ₃ L ₃ Cl ₂ |
| tBuDAB | 1:1 | Br | 231 | 399 | | |
| tBuDAB | 1:1 | BF ₄ | 231 | 399 | | |
| tBuDAB | 2:1 | Br | 231 | 399 | | |
| tBuDAB | 1:1 | Cl | - | 399 | 499 | 597 |
| iPrDAB | 1:1 | Br | 203 | 343 | | |
| tBuPCA | 1:1 | Br | 225 | 387 | | |
| tBuPCA | 1:1 | BF ₄ | 225 | 387 | | |
| tBuPCA | 1:1 | Cl | - | 387 | | |
| Bipy | 1:1 | Br | 300 | 456 | | |
| Bipy | 1:1 | BF ₄ | 219 | 375 | | |
| Bipy | 2:1 | BF ₄ | 219 | 375 | | |
| Bipy | 1:1 | Cl | - | 375 | | |

Bipy (Bipyridyl) is included as a comparison.

A crystal structure has been obtained for the reaction of tBu DAB and CuBr indicating a tetrahedral intermediate (Fig. 2).

Polymer Synthesis

5 The catalysts were used to control the propagation of styrene and methylmethacrylate. An effective catalyst should yield a polymer with a polydispersity of less than 1.5 and the Mn of the product increases with yield.

10 All polymerisations were performed with excess ligand 3:1 and the catalyst is synthesised in situ.

General method for polymerisation of methylmethacrylate

15 To a schlenk purged with nitrogen was added 0.54mls ethyl 2-bromo-isobutyrate (0.00372 mols) in 10mls methylmethacrylate (0.0935 mols). The desired ligand was then added (0.01122 mols) and the entire solution freeze pump thaw degassed. 0.536g copper bromide
20 (0.00374 mols) was then added whilst stirring. When the solution turned deep red indicating formulation of the catalyst the schlenk was immersed in an oil bath at 90°C.

POLYMERISATION RESULTS

All polymerisations are based on the following mole ratios.

Monomer : Initiator : Copper X : Ligand

100 : 1 : 1 : 3

Copper X = catalyst based on copper.

Styrene (Sty) was initiated with 1-phenylethyl bromide or chlorine.

Methylmethacrylate (MMA) was initiated with ethyl-2-bromo isobutyrate.

| ligand | mon. | X | t/hrs | T/C | Mn | Mw | PDI | Conv% |
|---------------------|------|----|-------|-----|--------|---------|------|-------|
| tBuDAB | STY | Br | 24 | 110 | 2,173 | 4,438 | 2 | 11 |
| iPrDAB | STY | Br | 24 | 110 | 1,975 | 72,587 | 38 | 5 |
| dimethylanilineDAB | STY | Br | 24 | 110 | 467 | 4,156 | 9 | 80 |
| tBuPCA | STY | Br | 24 | 110 | 338 | 1,110 | 3.2 | 1 |
| anilinePCA | STY | Br | 24 | 110 | 6,458 | 22,376 | 3.5 | 41 |
| dimethylaniline | STY | Br | 24 | 110 | 3,017 | 9,167 | 3 | 68 |
| tBuPCA | STY | Cl | 20 | 130 | 42,551 | 102,776 | 2.45 | 20 |
| nBuPCA | STY | Cl | 3 | 130 | 6,951 | 22,571 | 3.25 | 40 |
| iPrPCA | STY | Cl | 20 | 130 | 15,607 | 41,125 | 2.64 | 33 |
| anilinePCA | STY | Br | 20 | 110 | 6,458 | 22,376 | 4 | 41 |
| dimethylanilinePCA | STY | Br | 20 | 110 | 3,017 | 9,167 | 3 | 68 |
| isopropylanilinePCA | STY | Br | 20 | 130 | 3,700 | 10,074 | 2.72 | 61 |
| methoxyanilinePCA | STY | Br | 20 | 130 | 9,723 | 24,772 | 2.5 | 69 |
| anilinePCA | MMA | Br | 18 | 110 | 477 | 4,600 | 9.6 | 2 |
| dimethylanilinePCA | MMA | Br | 18 | 110 | 6,293 | 12,210 | 1.94 | 68 |
| nBuPCA | MMA | Br | 4 | 100 | 10,251 | 12,273 | 1.2 | 95 |
| nBuPCA | MMA | Br | 1 | 130 | 7,376 | 12,422 | 1.68 | - |
| nBuPCA | STY | Br | 40 | 80 | 5,492 | 7,313 | 1.33 | 43 |
| nBuPCA | STY | Br | 20 | 80 | 6,343 | 9,533 | 1.5 | 39 |

16

Polymerisation with tBuDAB

t-BuDAB was also investigated in more detail using different ratios of Ligand (L), Initiator (I) and catalyst (Cu).

Styrene at 100°C

| | <u>L:I</u> | <u>Cu:I</u> | <u>Mn</u> | <u>PDI</u> | <u>%Conv.</u> |
|----|------------|-------------|-----------|------------|---------------|
| 10 | 3 | 1 | 2173 | 2.0 | 11 |
| | 3 | 20 | 2603 | 4.0 | 7 |
| | 3 | 100 | 2169 | 5.8 | 8 |
| | 1 | 1 | 2400 | 3.6 | 9 |
| | 1 | 100 | 8042 | 14 | 7 |

15

MMA (100°C)

| | | | | |
|---|---|------|-----|-----|
| 3 | 1 | 2020 | 4.1 | Low |
|---|---|------|-----|-----|

20

This shows that PDI may be controlled by varying the ratio of L:I and/or Cu:I.

Polymerisations with nBuPCA

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The most successful ligand was nBuPCA which will form the following copper (I) structure:

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| | <u>TIME</u> | <u>% CONVERSION</u> | <u>Mn</u> | <u>PDI</u> |
|---|-------------|---------------------|-----------|------------|
| | 120 | 16.47 | 2376 | 1.28 |
| | 240 | 52.69 | 5249 | 1.22 |
| | 300 | 61.02 | 6232 | 1.18 |
| 5 | 360 | 67.56 | 6742 | 1.21 |
| | 485 | 78.56 | 7020 | 1.27 |

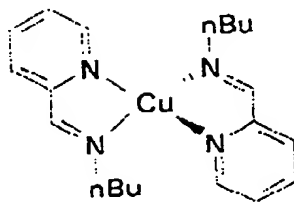
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moles) were added prior to 1.54mls of propylamine (1.11g, 1.873×10^{-4} moles). The reaction mixture immediately turns yellow. The mixture was stored for 10 minutes at room temperature prior to the addition of magnesium sulphate and stirring for a further 30 minutes. The reaction mixture was filtered and the volatile removed under reduced pressure. The product is isolated as a yellow oil.

10 Polymerisation

0.688g of copper (I) bromide (98% Aldrich) (4.796×10^{-4} moles) were added to 10mls of methylmethacrylate (purified by passage down a column containing basic alumina and 3A sieves under nitrogen (9.349×10^{-4} moles) in 20 mls of xylene (deoxygenated by 3 freeze-pump-thaw cycles and dried over 3A sieves for 12 hours). 0.2136g of A (1.44×10^{-4} moles) were added over 2 minutes with stirring at room temperature to give a homogenous deep red/brown solution. 0.07mls of ethyl 2-bromoisobutyrate (0.0924g, 4.73×10^{-4} moles) were added and the reaction mixture heated to 90°C for 485 minutes. Samples were taken at intervals and analysed for Mn and conversion, see table. After 485 minutes poly(methylmethacrylate) was isolated by precipitation into methanol in 78.6% yield with Mn = 7020 and PDI (M_w/M_n) = 1.27.

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5

This catalyst has been used to obtain kinetic data for the polymerisation of both styrene and methylmethacrylate. Temperature control is important to prevent termination leading to tailing of the resulting MW distribution. If termination is prevented then polydispersity will decrease with time. Mn conversion plots have been obtained at different monomer to initiator ratios.

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Figs. 3 and 4 show Mn dependence on conversion at different monomer:initiator for styrene and methylmethacrylate at 80°C.

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Fig. 5 shows Mw/Mn dependence on conversion for bulk polymerisation of styrene at 80°C.

Fig. 6 shows kinetic plots for the polymerisation of methylmethacrylate at 90°C.

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Synthesis of Block Co-polymers

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This was investigated using methylmethacrylate, benzylmethacrylate (BzMA) and 2 hydroxyethylmethacrylate (HEMA) the results of which are shown in the table below:

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TABLE B

| BLOCK ONE | | | | BLOCK TWO | | | | |
|-----------|-------|-------|------|-----------|-------|--------|------|-------|
| Mon. | Mn | Mw | PDI | Mon. | Mn | Mw | PDI | % MMA |
| MMA | 2,469 | 2,965 | 1.2 | MMA | 5,599 | 7,337 | 1.31 | 100 |
| MMA | 2,469 | 2,965 | 1.2 | BzMA | 4,908 | 6,500 | 1.32 | 70 |
| MMA | 2,499 | 3,431 | 1.37 | BzMA | 5,934 | 10,749 | 1.81 | 54 |
| MMA | 2,499 | 3,431 | 1.37 | HEMA | 3,298 | 5,544 | 1.68 | 70 |

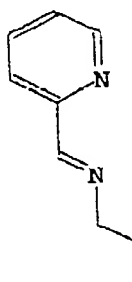
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Further experimentation

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Further experimentation was also carried out using ligands of Formula XII.

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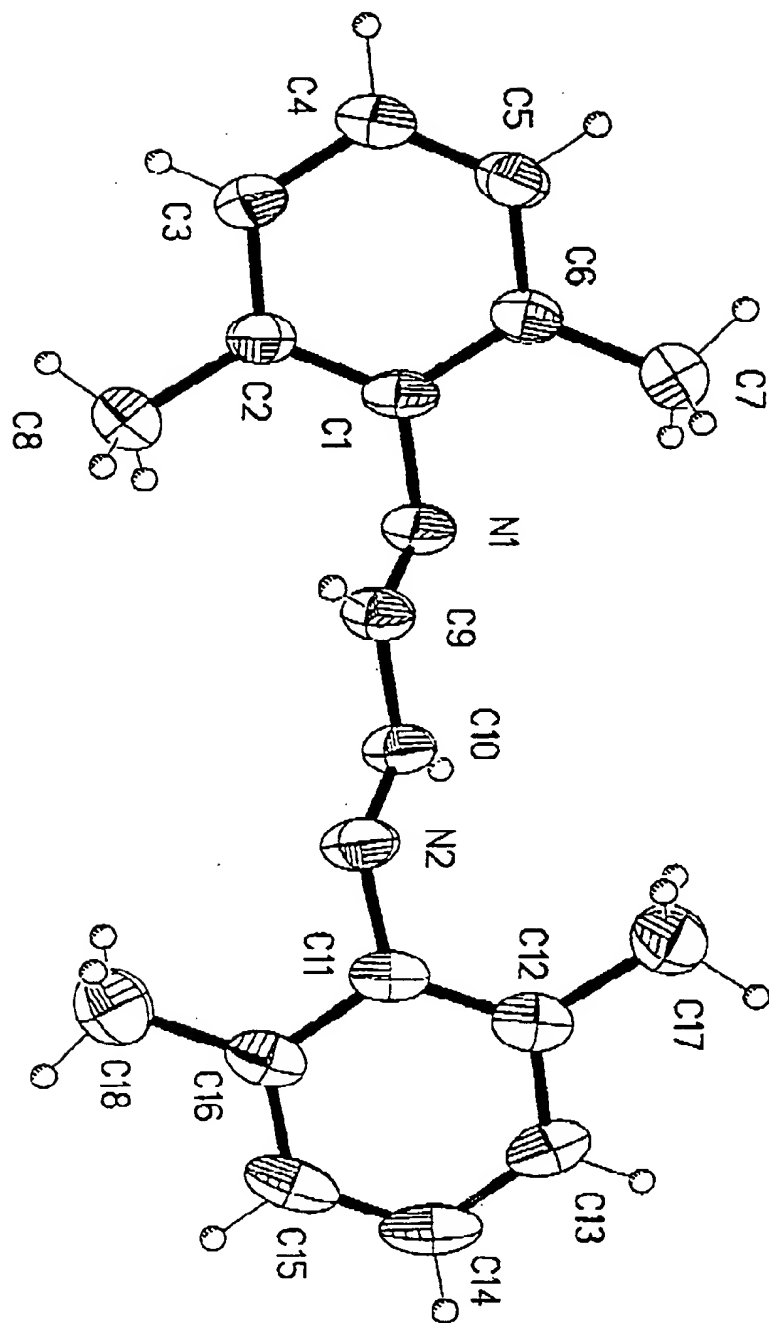


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This was synthesised as follows:

30mls of diethylether was placed in a conical flask.

1.78mls of 2-pyridine carbaldehyde (2.00g, 1.867×10^{-2}

Figure 1

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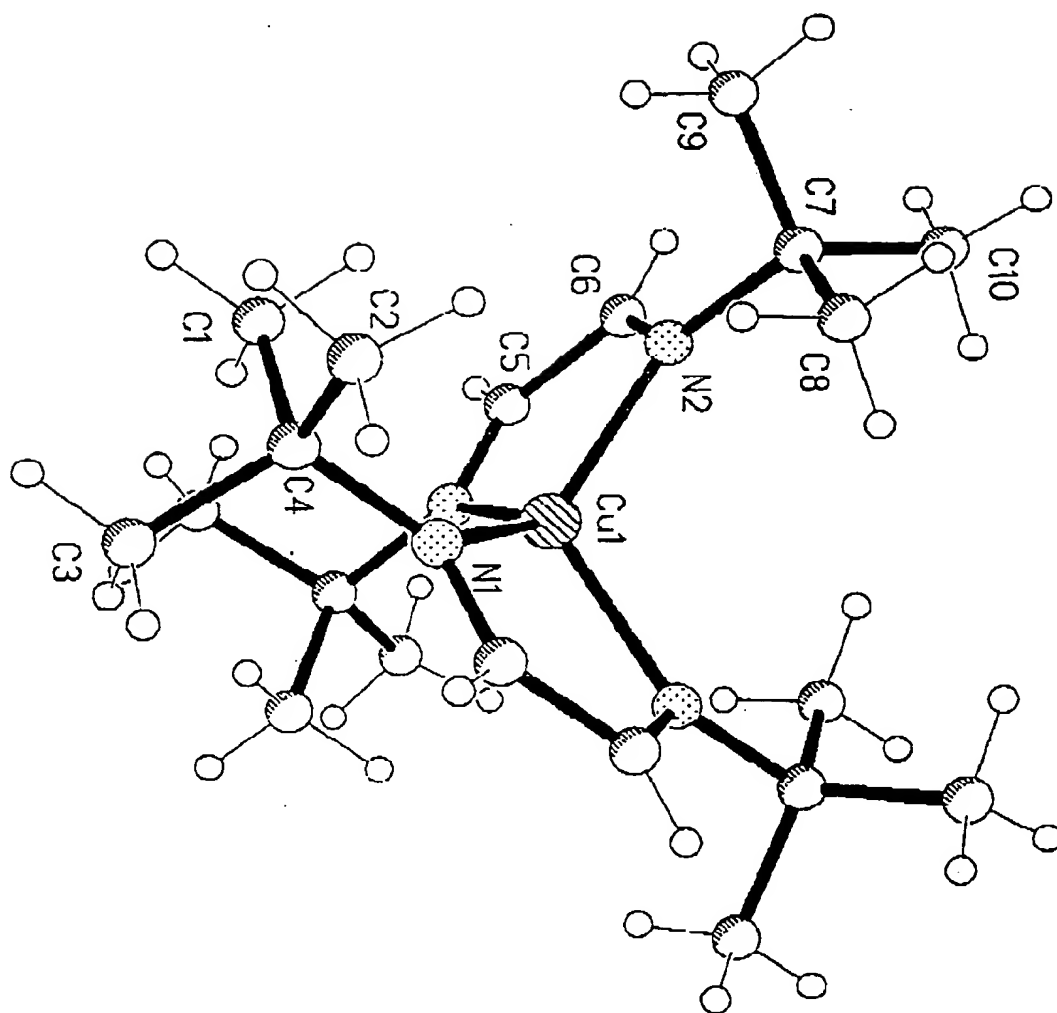


Figure 2

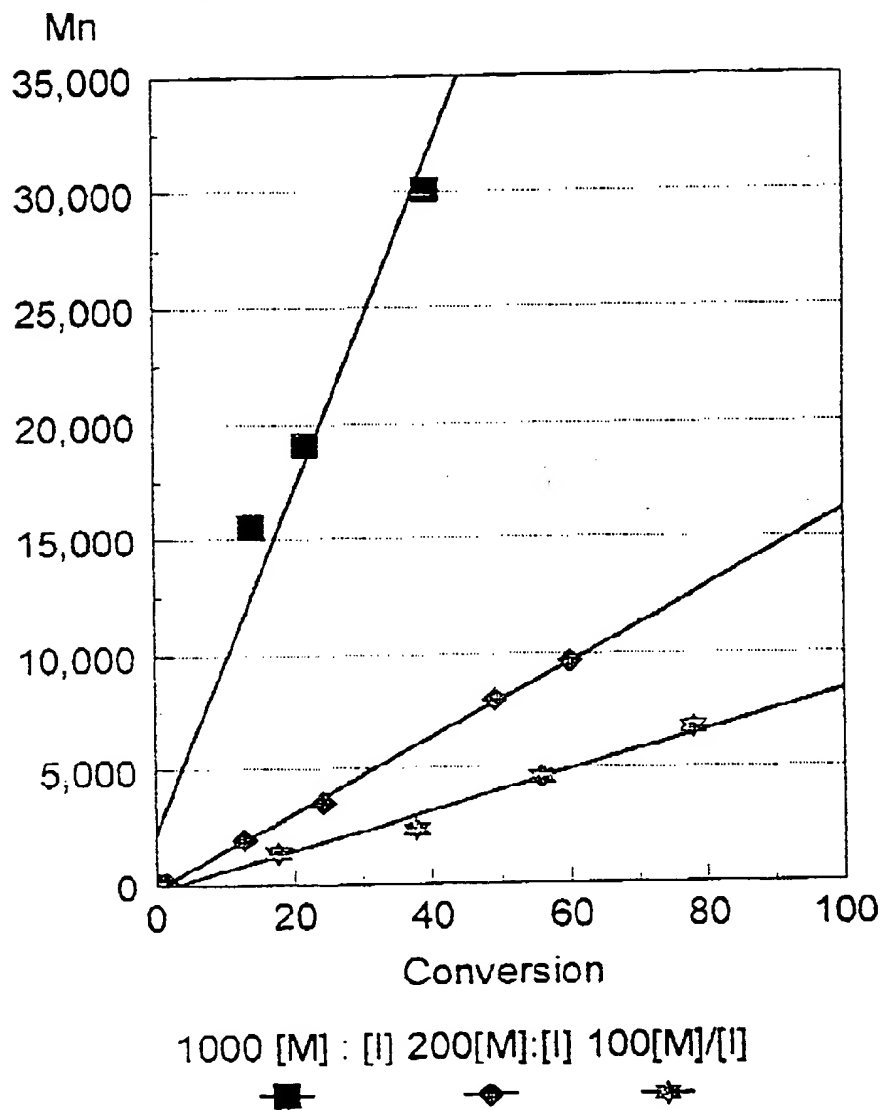
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Figure 3

Mn dependance on conversion

at different monomer: Initiator ratios

Polymerisation of styrene at 80C

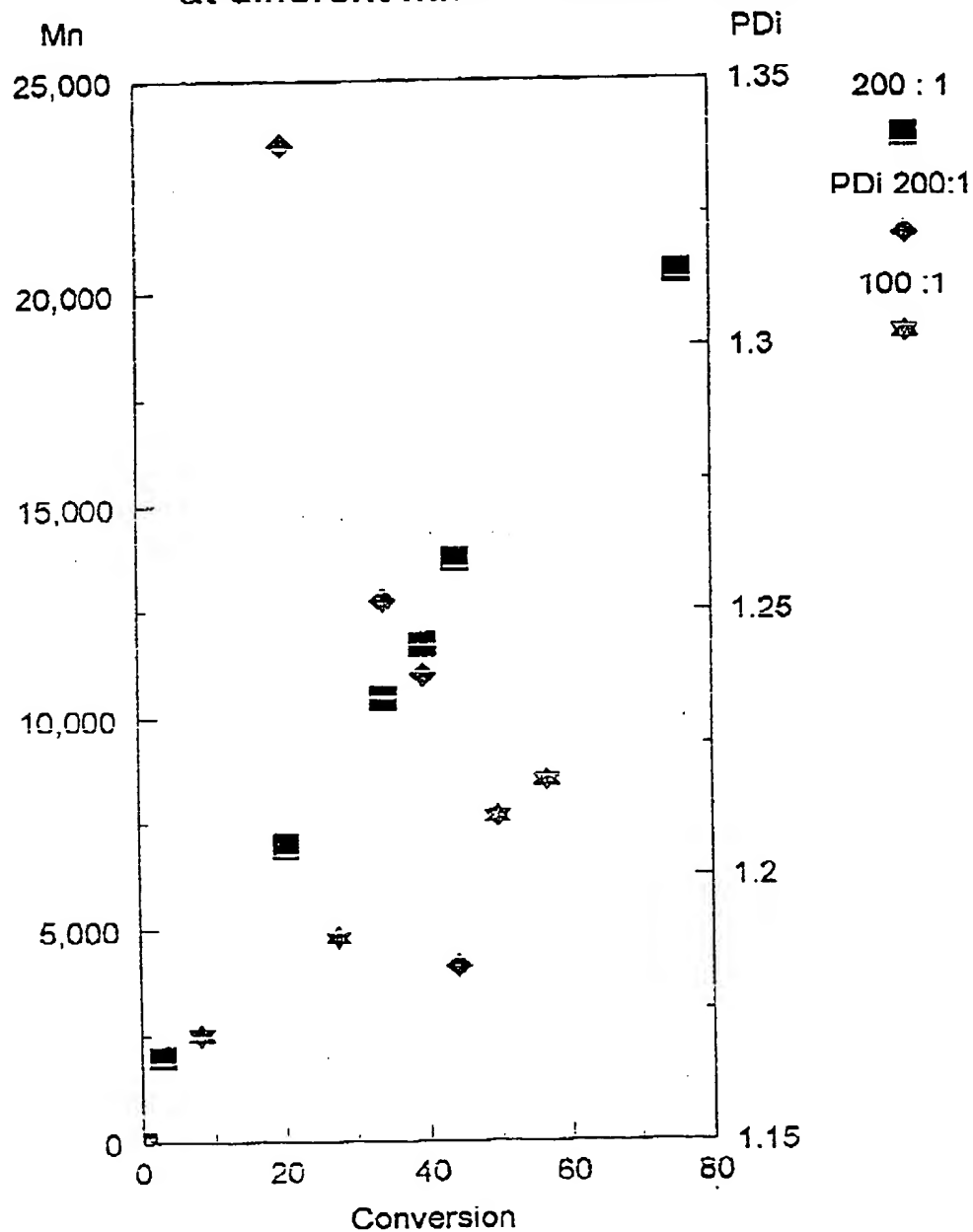


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Fig. 4.

Mn dependance on Conversion

at different MMA : Initiator ratios



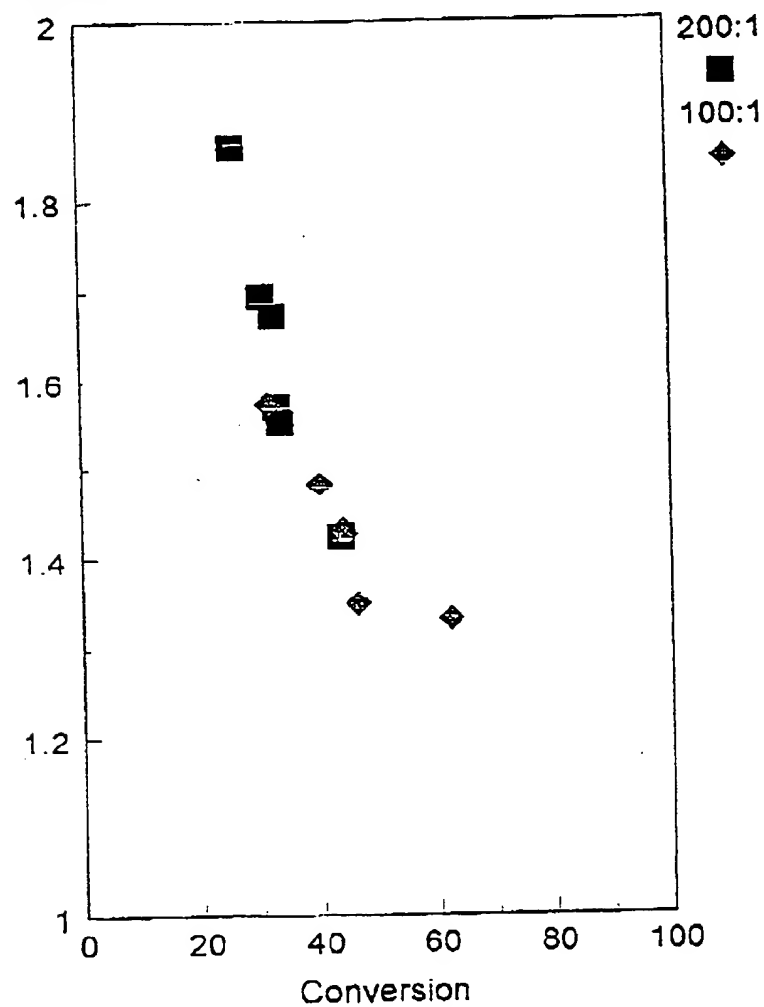
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Figure 5

Mw/Mn dependance on conversion

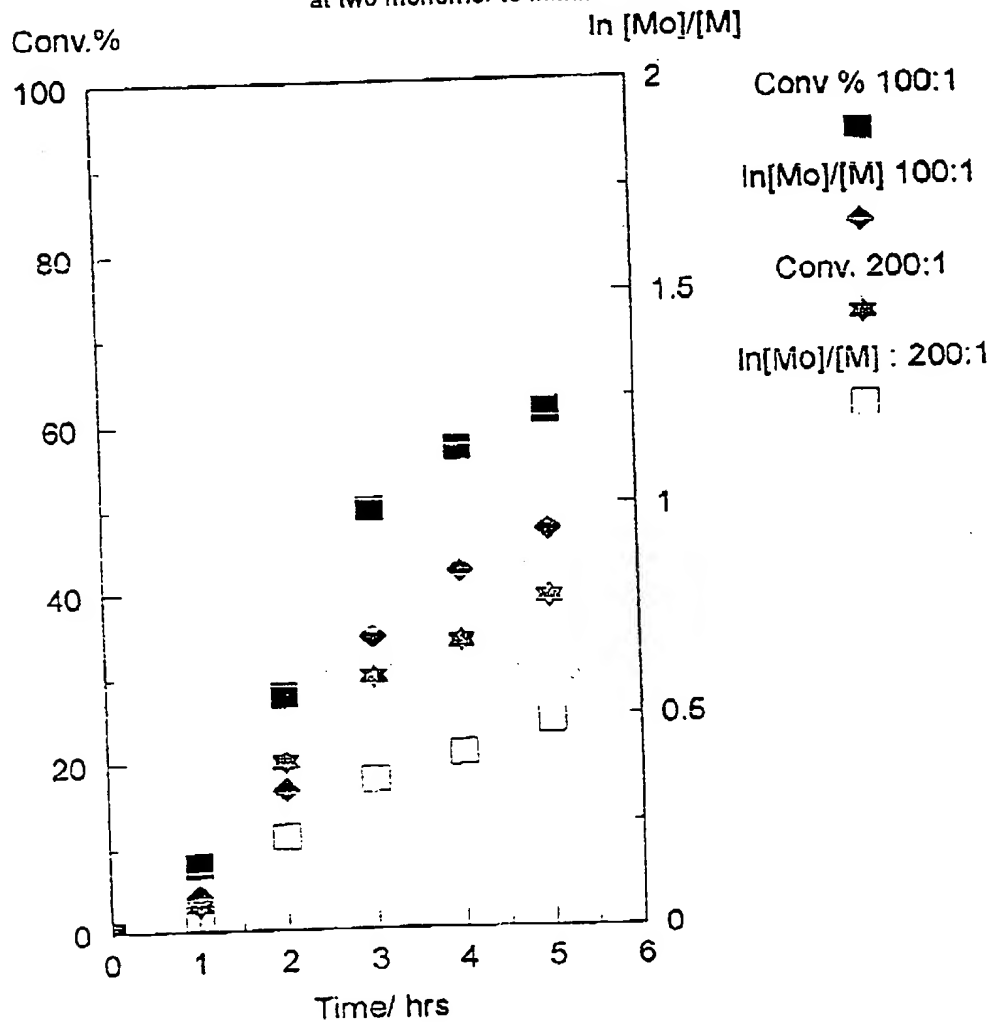
Bulk polymerisation of styrene at 80C

Mw/Mn



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Figure 6

KINETIC PLOTS FOR THE POLYMERISATION OF MMAPOLYMERISATION AT 90°C
at two monomer to initiator ratios

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